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Conical Energy Level Crossings in Molecular Dynamics

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Contents

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Part A

Setting the Stage

The crossing of energy levels has been a matter of considerable discussion.
(Clarence Zener, 1932)

The footnote explaining the introductory line of Zener's famous article on non-adiabatic crossings of energy levels refers to the work of Hund on molecular spectra and von Neumann's and Wigner's discussion of crossing eigenvalues in the context of adiabatic processes; see [Ze, Hun, NeWi]. Today, more than seventy years after the early days of quantum mechanics, mathematics has provided a considerable amount of methods and technique, which allows us to add a whisper to the discussion.

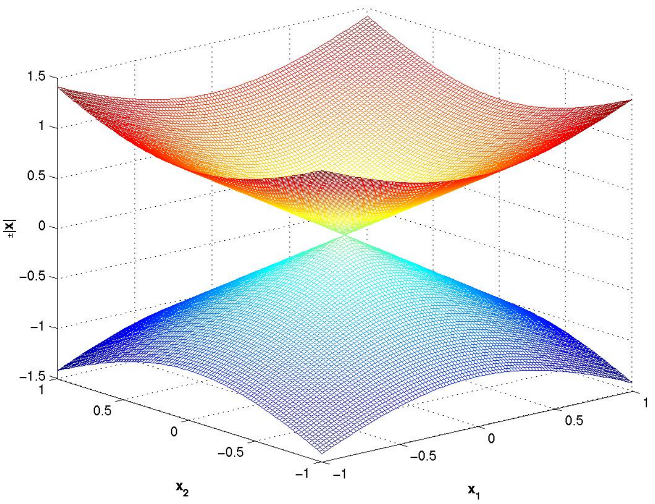
The core of this dissertation is a perhaps excessive case study of the following time-dependent Schrödinger system

$$\begin{aligned} i\,\varepsilon\,\partial_t\psi^\varepsilon(t,q) &= \left(-\tfrac{\varepsilon^2}{2}\Delta_q + V(q)\right)\psi^\varepsilon(t,q)\,, \\ \psi^\varepsilon(0,q) &= \psi_0^\varepsilon(q) \in L^2(\mathbb{R}^2,\mathbb{C}^2) \end{aligned} \tag{1}$$

with matrix-valued potential

$$V(q) = \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}, \qquad q = (q_1, q_2) \in \mathbb{R}^2$$

and small semi-classical parameter $\varepsilon > 0$. The eigenvalues of the matrix $V(q)$ are $E^\pm(q) = \pm|q|$ and meet at $q = 0$. Their joint graph shows two intersecting cones explaining the notion of a conical crossing.



The potential matrix $V(q)$ is a variant of Rellich's celebrated example

$$\begin{pmatrix} 1+2q_1 & q_1+q_2 \\ q_1+q_2 & 1+2q_2 \end{pmatrix}, \qquad (q_1, q_2) \in \mathbb{R}^2,$$

of a matrix, which depends smoothly on two parameters, but is not smoothly diagonizable; see §2 in [Re] and also Example 5.12 in Chapter II-§5.7 of [Ka]. A crossing of eigenvalues controlled by two parameters generates non-adiabatic transitions to leading order in the semi-classical parameter ε. The plots in Figure 1 nicely illustrate such a leading order non-adiabatic transition. The initial datum $\psi_0^\varepsilon(q)$ is a scalar Gaussian wave packet

$$g^\varepsilon(q) \;=\; (2\varepsilon\pi)^{-1/2}\,\exp(\,-\tfrac{1}{2\varepsilon}\,|q-q_0|^2 + \tfrac{i}{\varepsilon}\,p_0\cdot(q-q_0)\,) \tag{2}$$

times an eigenvector $\chi^+(q)$ of $V(q)$ with respect to the upper eigenvalue $E^+(q) = |q|$, that is $\psi_0^\varepsilon(q) = g^\varepsilon(q)\,\chi^+(q)$. Having not yet approached the crossing $\{q = 0\}$, the solution $\psi^\varepsilon(t,q)$ of the Schrödinger equation (1) is still a multiple of the upper eigenvector $\chi^+(q)$ to leading order in ε. However, near the crossing non-adiabatic transitions occur, and the solution $\psi^\varepsilon(t,q)$ also moves into the span of the lower eigenvector $\chi^-(q)$ to leading order in the parameter ε.

What's the new news of this dissertation ?

There's no news at the court, sir, but the old news ... The main new results are Theorem 8 and Theorem 10. The latter is easily formulated stating that the matrix-valued Schrödinger operator $H^\varepsilon = -\frac{\varepsilon^2}{2}\Delta_q + V(q)$ is of purely absolutely continuous spectrum, which covers the whole real line. Its proof relies on an orbital decomposition, an exact WKB construction, and subsequent application of the non-subordinacy method. It seems to be the first proof of such a result for an operator with an eigenvalue crossing. Theorem 8 does not have such a straightforward formulation. It provides an asymptotic description of the non-adiabatic dynamics of the Schrödinger system (1) by means of a semigroup acting on the initial datum's Wigner function. This semigroup stems from an underlying Markov process, which combines classical transport on the energy levels and jumps between the levels according to a Landau-Zener type formula. Its explicit construction entails an algorithm, which can be viewed as a rigorously derived counterpart of quantum chemistry's surface hopping algorithms.

The shoulders we have been standing on while working on this dissertation are the lecture notes [Bo] of F. Bornemann on homogenization, the book [DiSj] of M. Dimassi and J. Sjöstrand on semi-classical spectral asymptotics, the article [FeGe1] of C. Fermanian and P. Gérard on two-scale measures, the memoirs [Ha94] of G. Hagedorn on energy level crossings, L. Nédélec's article [Ne] on resonances, and the lecture notes [Te] of S. Teufel on adiabatic perturbation theory. The idea of the proof of Proposition 4, Figure 6, the definition of a two-scale Wigner functional, the examples for two-scale measures in Section 12.2, and Section's 12.5 replacement of I_{FG} by $\widetilde{I}_{FG}$ are taken from the joint publication [FeLa] with C. Fermanian. Most of the results in Part C have been obtained jointly with S. Teufel and can also be found in the preprint [LaTe]. The exact WKB construction of Section 16 will be used together with S. Fujiie and L. Nédélec for the derivation of Bohr-Sommerfeld conditions in [FLN].

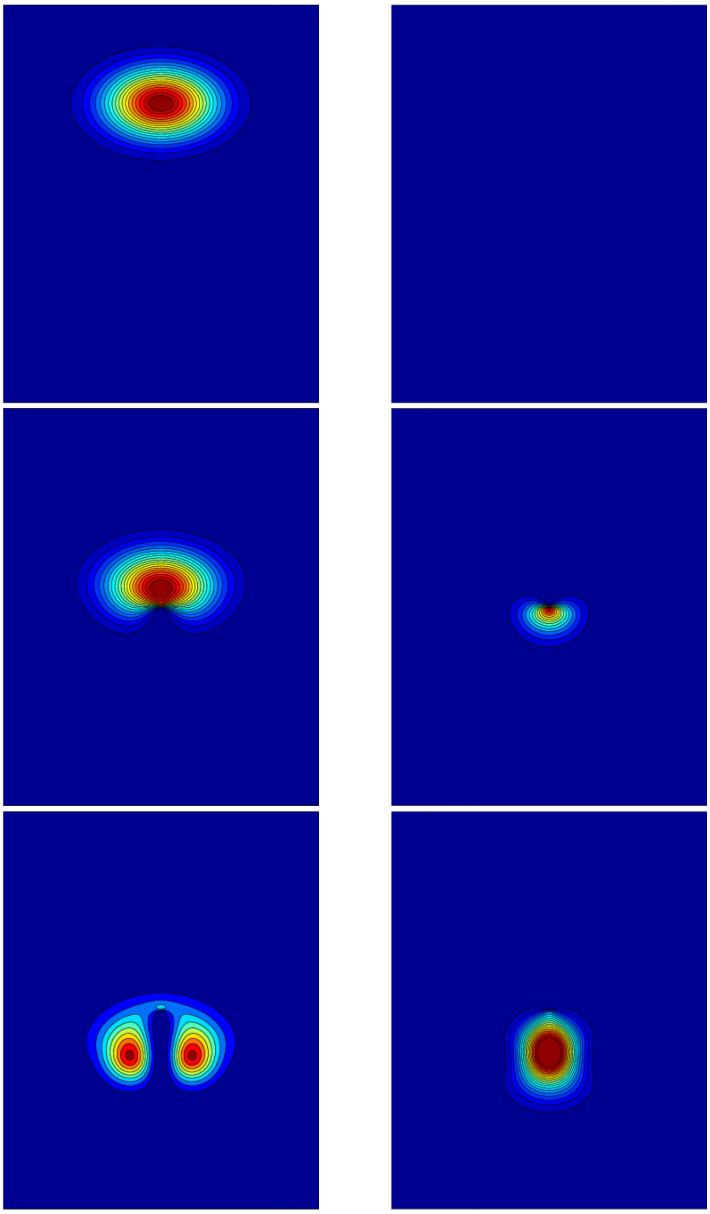


Figure 1: The plots show the energy populations for the propagation of a Gaussian wave function through the linear conical crossing. For initial data $\psi_0^\varepsilon(q) = g^\varepsilon(q)\chi^+(q)$ with g^ε and χ^+ as defined in (2) and (12), we have computed the solution $\psi^\varepsilon(t,q)$ of (1) by a Strang splitting algorithm. The plot shows $|\Pi^+(q)\psi^\varepsilon(t,q)|^2$ in the left column and $|\Pi^-(q)\psi^\varepsilon(t,q)|^2$ in the right column for times $t \in \left\{-2\sqrt{\varepsilon}, 0, 2\sqrt{\varepsilon}\right\}$, where $\Pi^\pm(q)$ are the eigen projectors of the potential matrix $V(q)$. The center (q_0, p_0) of the initial Gaussian has been chosen as $q_0 = (8\sqrt{\varepsilon}, 0)$ and $p_0 = (-1, 0)$ with semi-classical parameter $\varepsilon = 0.01$. We note, that the plots have been rotated by an angle of 90 degrees.

1 Essential Self-Adjointness

To establish existence and uniqueness of the solution to the Schrödinger equation (1), we study its Hamilton operator

$$H^\varepsilon \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_q + \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix} \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_q + V(q)\,. \tag{3}$$

Proposition 1 (Ess. Self-Adjointness) *For all $\varepsilon > 0$, the Hamiltonian H^ε is an essentially self-adjoint operator on $C_c^\infty(\mathbb{R}^2, \mathbb{C}^2)$.*

The following proof is analogous to the proof of the Faris-Lavine Theorem, Theorem X.38 in [ReSi2]. It is an application of Nelson's Commutator Theorem.

Proof. We set $N^\varepsilon = H^\varepsilon + 2|q|^2 + 2$ and choose $D(N^\varepsilon) = C_c^\infty(\mathbb{R}^2, \mathbb{C}^2)$. Since

$$\langle\, (V(q) + 2|q|^2 + 2)\, u, u \,\rangle \;\geq\; (-|q| + 2|q|^2 + 2)\, |u|^2 \;\geq\; |u|^2$$

for all $q \in \mathbb{R}^2$ and $u \in \mathbb{C}^2$, the operator N^ε is a Schrödinger operator with positive potential. Thus, N^ε is essentially self-adjoint on $D(N^\varepsilon)$. We also have

$$N^\varepsilon \;\geq\; 1\,, \qquad \|H^\varepsilon \phi\|_{L^2} \;\leq\; \|N^\varepsilon \phi\|_{L^2}$$

for all $\phi \in C_c^\infty(\mathbb{R}^2, \mathbb{C}^2)$. Moreover,

$$[H^\varepsilon,\, N^\varepsilon] \;=\; [-\tfrac{\varepsilon^2}{2}\,\Delta,\, 2|q|^2\,] \;=\; -2\varepsilon^2(q\cdot\nabla + \nabla\cdot q),$$

and since

$$-\tfrac{\varepsilon^2}{2}\Delta_q + |q|^2 \pm i\varepsilon\,(q\cdot\nabla + \nabla\cdot q) \;=\; (i\varepsilon\nabla \pm q)^2 \;\geq\; 0$$

we also have

$$\begin{aligned}
\langle N^\varepsilon \phi, \phi\rangle_{L^2} \;&\geq\; \Big\langle \big(-\tfrac{\varepsilon^2}{2}\,\Delta_q + |q|^2\big)\,\phi, \phi\,\Big\rangle_{L^2} \;\geq\; \varepsilon\,|\,\langle (q\cdot\nabla + \nabla\cdot q)\,\phi, \phi\rangle_{L^2}\,| \\
&=\; \tfrac{1}{2\varepsilon}\,|\,\langle\, [H^\varepsilon, N^\varepsilon]\,\phi, \phi\,\rangle\,|
\end{aligned}$$

for $\phi \in C_c^\infty(\mathbb{R}^2, \mathbb{C}^2)$. Hence, we are done by applying Nelson's Commutator Theorem. □

Remark 1 The previous proof also applies to more general Schrödinger systems, as long as the potential $V(q)$ is a symmetric matrix such that there exists a constant $C > 0$ with

$$\langle V(q)u, u\rangle \geq -C\,|q|\,|u|$$

for all $q \in \mathbb{R}^2$ and all $u \in \mathbb{C}^2$. ♢

Given essential self-adjointness of the Hamiltonian, the spectral theorem immediately yields the desired existence and uniqueness result. Here and in the following, we will use the operator H^ε also in places where the operator's closure $\overline{H^\varepsilon}$ would have been more correct.

Corollary 1 *For arbitrary initial data* $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$, *the Schrödinger system (1) has a unique global solution*

$$e^{-iH^\varepsilon t/\varepsilon}\psi_0^\varepsilon =: \psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2)).$$

Having established well-posedness of our favourite model system, we turn to the question how it relates to molecular dynamics.

2 Born-Oppenheimer Approximation

In molecules, the mass discrepancy between the heavy nuclei and the light electrons causes dynamics associated with two different time-scales: the nuclei move slowly, more or less like classical particles, while the electrons perform a rapid oscillatory motion. How is this intuitive picture formulated in mathematical terms? Neglecting spin degrees of freedom and relativistic effects, one describes the full quantum-mechanical motion of a molecule by the time-dependent Schrödinger equation

$$i\partial_\tau \psi = H_{\mathrm{mol}}\,\psi, \qquad \psi(0) = \psi_0 \tag{4}$$

with a square-integrable initial datum $\psi_0 = \psi_0(x, X) \in L^2(\mathbb{R}^{3(n+N)}, \mathbb{C})$. The vector $x = (x_1, \dots, x_n) \in \mathbb{R}^{3n}$ contains the positions of the n electrons, and $X = (X_1, \dots, X_N) \in \mathbb{R}^{3N}$ the positions of the N nuclei. In atomic units, the full molecular Hamiltonian

$$\begin{aligned} H_{\mathrm{mol}} &= -\sum_{j=1}^{n} \tfrac{1}{2}\,\Delta_{x_j} - \sum_{j=1}^{N} \tfrac{1}{2M_j}\,\Delta_{X_j} \\ &+ \sum_{j<k} |x_j - x_k|^{-1} + \sum_{j<k} Z_j\, Z_k\, |X_j - X_k|^{-1} - \sum_{j,k} Z_k\, |x_j - X_k|^{-1} \end{aligned}$$

consists of electronic and nucelonic kinetics, Coulomb interaction inbetween electrons, inbetween nuclei, and between electrons and nuclei. $Z_j > 0$ and $M_j > 0$ denote the charge and the mass of the jth nucleus, respectively. By Kato's Theorem, see Theorem 1 in [Ka51], the molecular Hamiltonian H_{mol} is self-adjoint with domain $H^2(\mathbb{R}^{3(n+N)}, \mathbb{C})$, and the spectral theorem gives existence and uniqueness of the solution of the Cauchy problem (4),

$$\psi(\tau) = e^{-i\tau H_{\mathrm{mol}}}\psi_0 \in C(\mathbb{R}, L^2(\mathbb{R}^{3(n+N)}, \mathbb{C})).$$

2.1 Adiabatic Decoupling

Departing from the elegance of existence and uniqueness questions, one has to realize, however, that even for common molecules like carbondioxide CO_2, which is built of three nuclei and 22 electrons, the full quantum mechanical description is cursed by the high dimensionality of the molecular configuration space $\mathbb{R}^{3(n+N)}$. For carbondioxide, one would a priori have to deal with wave functions acting on $\mathbb{R}^{75}$. Hence, one is striving for a considerable reduction of degrees of freedom, which is provided by the time-dependent Born-Oppenheimer approximation first undertaken by G. Hagedorn in [Ha80]. For a precise formulation of this important approximation we switch from $L^2(\mathbb{R}^{3(n+N)}, \mathbb{C})$ to the isomorphic space

$$\mathcal{H} := \int_{\mathbb{R}^{3N}}^{\oplus} L^2(\mathbb{R}^{3n}, \mathbb{C})\, dX = L^2(\mathbb{R}^{3N}, \mathbb{C}) \otimes L^2(\mathbb{R}^{3n}, \mathbb{C})$$

and rewrite the full molecular Hamiltonian H_{mol} as

$$H^{\varepsilon}_{\text{mol}} = -\tfrac{\varepsilon^2}{2} \Delta_X \otimes \mathbb{1}_{L^2(\mathbb{R}^{3n}, \mathbb{C})} + H_{\text{el}}\,.$$

The small parameter $\varepsilon > 0$ already indicates, that from now on we only consider molecules with nuclei of identical mass $M_j = \varepsilon^{-2}$. For real life's molecules we may expect

$$10^{-3} \lesssim \varepsilon \lesssim 10^{-2}\,.$$

The part of the full molecular operator, which depends on the electronic degrees of freedom, the so-called electronic Hamiltonian, is the fibered operator

$$H_{\text{el}} = \int_{\mathbb{R}^{3N}}^{\oplus} H_{\text{el}}(X)\, dX\,.$$

Inside the fiber operators

$$\begin{aligned} H_{\text{el}}(X) &= -\sum_{j=1}^{n} \tfrac{1}{2} \Delta_{x_j} + \sum_{j<k} |x_j - x_k|^{-1} \\ &+ \sum_{j<k} \int_{\mathbb{R}^6} \rho(y - X_j)\, \rho(y' - X_k)\, |y - y'|^{-1}\, dy\, dy' - \sum_{j,k} \int_{\mathbb{R}^3} \rho(y - X_j)\, |y - x_k|^{-1}\, dy \end{aligned}$$

the Coulomb interaction inbetween nuclei as well as between nuclei and electrons is smeared out by means of a charge density $\rho \in C_c^{\infty}(\mathbb{R}^3, [0, \infty[)$. This suppression of Coulomb interaction is a technical necessity providing us with smooth dependance of the fiber operators $H_{\text{el}}(X)$ on the nucleonic configuration $X \in \mathbb{R}^{3N}$, that is

$$(H_{\text{el}}(\cdot) - i)^{-1} \in C_b^{\infty}(\mathbb{R}^{3N}, \mathcal{L}(L^2(\mathbb{R}^{3n}, \mathbb{C})))\,. \tag{5}$$

Imposing this form of regularity draws from Chapter 1 and Chapter 2.3 of the monographs [Ha94] and [Te], respectively, which assume the mapping $X \mapsto (H_{\text{el}}(X) - i)^{-1}$ to be k-times differentiable for suitable $2 \leq k \leq \infty$. With or without Coulomb interaction, the fiber operators $H_{\text{el}}(X)$ are for all $X \in \mathbb{R}^{3N}$ infinitesimally operator bounded with respect to the Laplacian in $L^2(\mathbb{R}^{3n}, \mathbb{C})$, see Lemma 4 in [Ka51]. Hence, we have as the domain of self-adjointess for the full electronic Hamiltonian H_{el}

$$D(H_{\text{el}}) = \left\{ \psi \in \mathcal{H} \mid \psi(X) \in H^2(\mathbb{R}^{3n}, \mathbb{C}) \text{ a.e.}, \int_{\mathbb{R}^{3N}} \|\psi(X)\|^2_{H^2(\mathbb{R}^{3n})} < \infty \right\},$$

see Theorem XIII.85 in [ReSi4]. The full molecular Hamiltonian $H^{\varepsilon}_{\text{mol}}$ is then essentially self-adjoint on

$$D(H^{\varepsilon}_{\text{mol}}) = H^2(\mathbb{R}^{3N}, \mathbb{C}) \otimes L^2(\mathbb{R}^{3n}, \mathbb{C}) \cap D(H_{\text{el}})\,.$$

Let $X \in \mathbb{R}^{3N}$. One expects for the spectrum $\sigma(H_{el}(X))$ of the electronic fiber Hamiltonian the following situation. The essential spectrum

$$\sigma_{ess}(H_{el}(X)) \;=\; [\Sigma(X), \infty[$$

is an unbounded interval, where $\Sigma(X)$ is something like the minimal energy, which the electronic system can have after being broken into two pieces. This cloudy formulation tries to verbalize the HVZ Theorem, see Theorem XIII.17 in [ReSi4]. Since $H_{el}(X)$ is bounded from below, see the remark before Theorem 1 in [Ka51], the discrete spectrum

$$\sigma_{disc}(H_{el}(X)) \;=\; \{E_1(X) \;\leq\; E_2(X) \;\leq\; E_3(X)\ldots\}$$

is a finite or countably infinite set with $\Sigma(X)$ as a possible accumulation point. As an example, see the spectra of nitrogen N_2 in Figure 2. Let $\Lambda \subseteq \mathbb{R}^{3N}$ be an open subset of $\mathbb{R}^{3N}$ and $f_\pm \in C(\Lambda, \mathbb{R})$ two continuous functions with

$$\forall X \in \Lambda: \quad f_-(X) < f_+(X)\,,\; f_\pm(X) \notin \sigma(H_{el}(X))\,. \tag{6}$$

Let for $X \in \Lambda$ be $\sigma_*(X) \subset \sigma(H_{el}(X))$ a subset of the electronic spectrum, which is contained in the interval $[f_-(X), f_+(X)]$, such that

$$\exists\, g > 0\ \forall X \in \Lambda: \quad \mathrm{dist}([f_-(X), f_+(X)], \sigma(H_{el}(X)) \setminus \sigma_*(X)) \;\geq\; g\,. \tag{7}$$

Having the spectra of nitrogen in mind, the case $\Lambda = \mathbb{R}^{3N}$ would mean that $\sigma_*(X)$ contains the electronic ground state energy only, since only at the bottom of the spectrum we expect a global spectral gap. For $\Lambda \subsetneq \mathbb{R}^{3N}$, however, there are plenty of possible choices for the set $\sigma_*(X)$. We denote by $P_*(X) \in \mathcal{L}(L^2(\mathbb{R}^{3n}, \mathbb{C}))$ the spectral projection of $H_{el}(X)$ onto the spectral subspace associated with $\sigma_*(X)$. Having assumed the existence of a spectral gap $g > 0$, the projectors inherit the smooth dependance on the nucleonic configuration from the electronic fiber Hamiltonians.

Lemma 1 *We have* $P_*(\cdot) \in C_b^\infty(\Lambda, \mathcal{L}(L^2(\mathbb{R}^{3n}, \mathbb{C})))$, *and hence* $\dim \mathrm{Ran}(P_*(\cdot)) = \mathrm{const.}$ *If in the special case* $\dim \mathrm{Ran}(P_*(\cdot)) = 1$ *we denote* $\sigma_*(X) =: \{E(X)\}$, *then* $E(\cdot) \in C_b^\infty(\Lambda, \mathbb{R})$.

Proof. Let $Y \in \Lambda$. By Riesz' formula, see II-§1.4 and VI-§5.4 in [Ka],

$$P_*(Y) \;=\; \frac{i}{2\pi} \int_{\Gamma(Y)} (H_{el}(Y) - \zeta)^{-1}\, d\zeta\,,$$

where $\Gamma(Y) \subset \mathbb{C}$ is a closed positively oriented curve with $\Gamma(Y) \cap \sigma(H_{el}(Y)) = \emptyset$, which encloses only $\sigma_*(Y)$ but no other elements of $\sigma(H_{el}(Y))$. Such a curve exists because of the gap $g > 0$. We have continuity of the resolvent, see (5), and of the functions $f_\pm$. Hence, there exists a neighbourhood $U(Y) \subset \Lambda$ of Y, such that $\Gamma(Y) \cap \sigma(H_{el}(X)) = \emptyset$ and the curve $\Gamma(Y)$ encloses only $\sigma_*(X)$ but no other points of $\sigma(H_{el}(X))$ for all $X \in U(Y)$. Therefore, for all $X \in U(Y)$

$$P_*(X) \;=\; \frac{i}{2\pi} \int_{\Gamma(Y)} (H_{el}(X) - \zeta)^{-1}\, d\zeta\,,$$

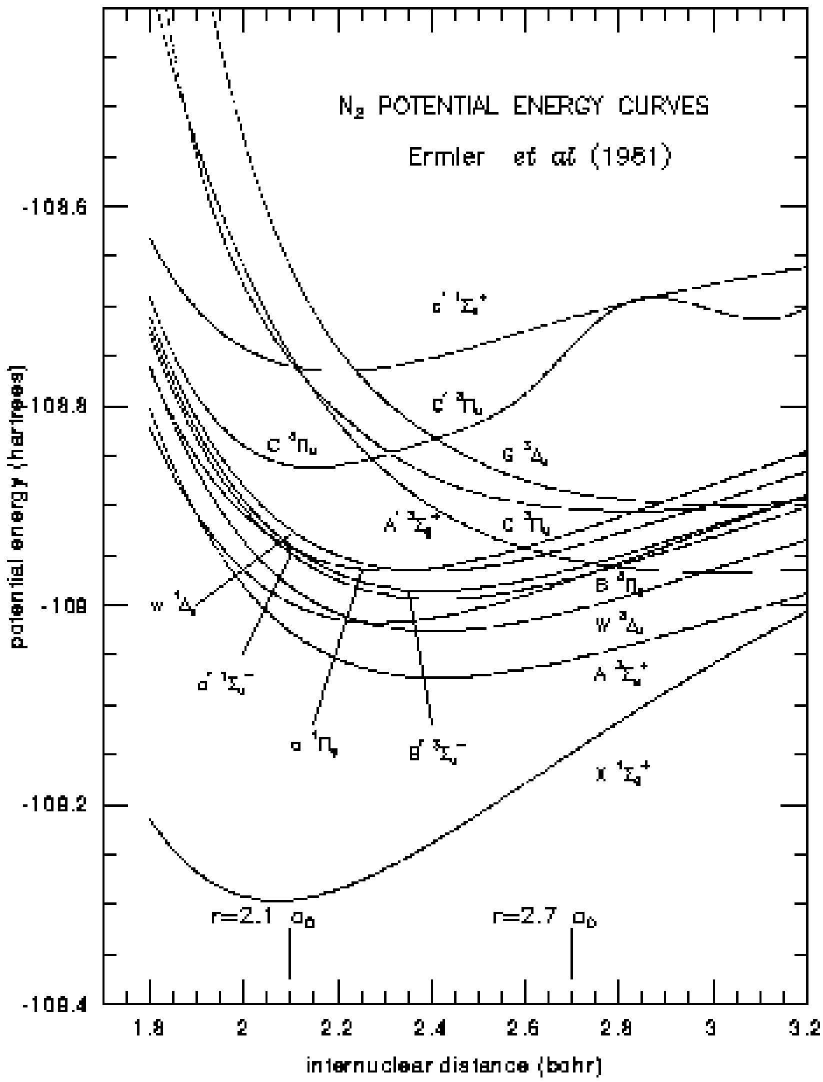


Figure 2: Spectrum of the electronic fiber Hamiltonians of nitrogen N_2 as a function of the distance between the two nuclei. The plot is taken from [GTLB]. The annotation of the ordinate refers to the elements of the electronic spectrum as potential energies.

is indeed the projection of $H_{el}(X)$ onto the spectral subspace associated with $\sigma_*(X)$. From this representation of $P_*(\cdot)$ on $U(Y)$, we immediately deduce the claimed smoothness and boundedness of $P_*(\cdot)$ on Λ. If $\dim \mathrm{Ran}(P_*(\cdot)) = 1$, then $E(\cdot) = \mathrm{tr}(H_{el}(\cdot)P_*(\cdot))$, which implies the claimed properties of $E(\cdot)$, since

$$H_{el}(X)\, P_*(X) \;=\; \frac{i}{2\pi} \int_{\Gamma(Y)} \zeta\, (H_{el}(X) - \zeta)^{-1}\, d\zeta \;\in\; \mathcal{L}(L^2(\mathbb{R}^{3n}, \mathbb{C}))$$

for all $X \in U(Y)$, see III-§6.4 in [Ka]. □

The operator

$$P_* \;:=\; \int_{\mathbb{R}^{3N}}^{\oplus} P_*(X)\, dX \;\in\; \mathcal{L}(\mathcal{H})$$

is an orthogonal projection, but in general *no spectral* projection for the electronic Hamiltonian H_{el}. The fiber projectors commute with the fiber electronic Hamiltonians, that is $P_*(X)H_{el}(X) \subset H_{el}(X)P_*(X)$ for all $X \in \mathbb{R}^{3N}$, see for example Theorem 6.17 in [Ka]. Hence, also P_* commutes with H_{el}, which in turn implies the invariance of $\mathrm{Ran}(P_*)$ under H_{el}, meaning $H_{el}\, \mathrm{Ran}(P_*) \subset \mathrm{Ran}(P_*)$. We also have invariance of the band subspace $\mathrm{Ran}(P_*)$ under the strongly continuous one-parameter group $(e^{-i\tau H_{el}})_{\tau \in \mathbb{R}}$, as the following Lemma easily proves.

Lemma 2 (Invariance) *We have* $e^{-i\tau H_{el}}\, \mathrm{Ran}(P_*) \subset \mathrm{Ran}(P_*)$ *for all* $\tau \in \mathbb{R}$.

Proof. We just work on the domain $D(H_{el})$ and conclude then by density. Clearly, $e^{-i\tau H_{el}}\, P_* = [e^{-i\tau H_{el}}, P_*] + P_*\, e^{-i\tau H_{el}}$. Hence, we are done, if we show that the commutator vanishes. Indeed,

$$\left[e^{-i\tau H_{el}}, P_*\right] \;=\; \int_0^\tau \tfrac{d}{ds} \left(e^{-i s H_{el}}\, P_*\, e^{i(s-\tau) H_{el}}\right) ds \;=\; i \int_0^\tau e^{-i s H_{el}}\, [P_*, H_{el}]\, e^{i(s-\tau) H_{el}}\, ds \;=\; 0\,.$$

□

Since we can view the full molecular Hamiltonian H^ε_{mol} as a perturbation of the electronic Hamiltonian H_{el}, we may ask the natural question, whether the band subspace $\mathrm{Ran}(P_*)$ also has some invariance properties under the time evolution associated with the full Hamiltonian H^ε_{mol}. Because $-\frac{\varepsilon^2}{2}\Delta_X$ is a singular perturbation of H_{el}, the answer of this question requires substantial mathematical insight, and we find it in the framework of time-dependent Born-Oppenheimer approximation. Let $\lambda \in \mathbb{R}$ and $\mathbb{1}_{]-\infty,\lambda]}(H^\varepsilon_{mol}) \in \mathcal{L}(\mathcal{H})$ be the projection onto states with energies smaller than λ. If one assumes a global gap condition, that is $\Lambda = \mathbb{R}^{3N}$, then

$$\left\| \left(e^{-i H^\varepsilon_{mol} t/\varepsilon} - e^{-i P_* H^\varepsilon_{mol} P_* t/\varepsilon}\right) P_*\, \mathbb{1}_{]-\infty,\lambda]}(H^\varepsilon_{mol}) \right\|_{\mathcal{L}(\mathcal{H})} \;\le\; \text{const.}\, \varepsilon\, (1 + |t|) \qquad (8)$$

for all $t \in \mathbb{R}$ and $\varepsilon > 0$. This is the formulation of time-dependent Born-Oppenheimer approximation due to H. Spohn and S. Teufel, see Theorem 1 in [SpTe]. It is important to notice, that the above approximation applies to the time-dependent Schrödinger equation

$$i\,\varepsilon\, \partial_t \psi \;=\; H^\varepsilon_{mol}\, \psi\,, \qquad \psi(0) \;=\; \psi_0\,, \qquad (9)$$

which is formulated with respect to the *slow* nucleonic time-scale. That is, the time-scale of the original Schrödinger equation (4) has been changed by replacing $\tau \mapsto t = \tau/\varepsilon$. In particular, inequality (8) also answers the raised invariance question: it implies

$$\left\| \left[e^{-i H^{\varepsilon}_{\mathrm{mol}} t/\varepsilon}, P_* \right] \mathbb{1}_{]-\infty,\lambda]}(H^{\varepsilon}_{\mathrm{mol}}) \right\|_{\mathcal{L}(\mathcal{H})} \leq \text{const.}\, \varepsilon\, (1 + |t|)\,,$$

that is *almost invariance* in the case of finite total energies. Alternatively, one refers to $\mathrm{Ran}(P_*)$ as an adiabatically decoupled or adiabatically protected subspace, where the notion *adiabatic* stems from the Greek word *adiabatos* meaning "not passing through".

2.2 Born-Oppenheimer Hamiltonians

Having obtained an almost decoupling of the band subspace $\mathrm{Ran}(P_*)$, one might ask for more concrete information about the dynamics inside this subspace. Addressing this issue in the following, we will work for the special case when the fiber projectors $P_*(X)$ are of finite rank, that is $\dim \mathrm{Ran}(P_*(X)) = m \in \mathbb{N}$ for all $X \in \mathbb{R}^{3N}$, and the associated spectral subset $\sigma_*(X)$ is separated from the remainder of the spectrum by a global gap $g > 0$ in the sense of the previous section. Such a spectral subset can be written as

$$\sigma_*(X) = \{E_1(X), \ldots, E_m(X)\} \qquad \text{for all } X \in \mathbb{R}^{3N}\,,$$

where $E_1(X) \leq \ldots \leq E_m(X)$ are m repeated eigenvalues of $H_{\mathrm{el}}(X)$. There is a numbering of these repeated eigenvalues, such that the mappings $\mathbb{R}^{3N} \mapsto \mathbb{R}$, $X \mapsto E_j(X)$ are Lipschitz continuous, see II-§5.7 and IV-§3.5 in [Ka]. More regularity, however, can only be guaranteed in the case of a constantly degenerate m-fold eigenvalue, that is, if $E_1(X) = \ldots = E_m(X)$ for all $X \in \mathbb{R}$. Looking in the electronic spectra of real life's molecules for subsets, which are globally isolated from the remainder of the spectrum, one will find

$$\sigma_*(X) = \{E(X)\} \qquad \text{for all } X \in \mathbb{R}^{3N}\,,$$

where $E(X)$ is the simple eigenvalue at the bottom of the spectrum of $H_{\mathrm{el}}(X)$, the ground state energy. The spectral plot of nitrogen in Figure 2 illustrates this fact very clearly. Nevertheless, we admit general finite $m \in \mathbb{N}$. Since $P_*(\cdot) \in C^\infty_b(\mathbb{R}^{3N}, \mathcal{L}(L^2(\mathbb{R}^{3n}, \mathbb{C})))$, there exist $\chi_j \in C^\infty_b(\mathbb{R}^{3N}, L^2(\mathbb{R}^{3n}, \mathbb{C}))$ such that $\{\chi_j(X) \mid j = 1, \ldots, m\}$ is an orthonormal basis of $\mathrm{Ran}(P_*(X))$ for all $X \in \mathbb{R}^{3N}$. Since the $\chi_j(X)$ are normalized functions, we have $\mathrm{Re}\,\langle \chi_j(X), \nabla_X \chi_j(X)\rangle_{L^2(\mathbb{R}^{3n})} = 0$ for all $X \in \mathbb{R}^{3N}$. Moreover, since $\mathbb{R}^{3N}$ is contractible, we can also ensure that

$$\mathrm{Im}\,\langle \chi_j(X), \nabla_X \chi_j(X)\rangle_{L^2(\mathbb{R}^{3n})} = 0 \qquad \text{for all } X \in \mathbb{R}^{3N}$$

by applying a smooth gauge transformation $\chi_j(X) \mapsto e^{i\theta(X)}\chi_j(X)$ if necessary. By means of the function $\chi(\cdot) = (\chi_1(\cdot), \ldots, \chi_m(\cdot))^t$ we write

$$\mathrm{Ran}(P_*) = \left\{ \int^{\oplus}_{\mathbb{R}^{3N}} \phi(X) \cdot \chi(X)\, dX \;\middle|\; \phi \in L^2(\mathbb{R}^{3N}, \mathbb{C}^m) \right\}.$$

The mapping

$$U:\ \mathrm{Ran}(P_*) \to L^2(\mathbb{R}^{3N}, \mathbb{C}^m)\,, \quad U(\phi \cdot \chi) = \phi$$

then defines an isometry, which translates the possibly very complicated band subspace $\mathrm{Ran}(P_*) \subset \mathcal{H}$ into the more manageable Hilbert space $L^2(\mathbb{R}^{3N}, \mathbb{C}^m)$. In the reference space $L^2(\mathbb{R}^{3N}, \mathbb{C}^m)$ one defines the Born-Oppenheimer Hamiltonian

$$H^\varepsilon_{\mathrm{BO}} \;:=\; -\tfrac{\varepsilon^2}{2}\,\Delta_X + V(X)\,,$$

where $V(\cdot) \in C_b^\infty(\mathbb{R}^{3N}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^m))$ is a smooth function with values in the space of hermitian $m \times m$-matrices with components

$$V(X)_{j,k} \;=\; \langle\, H_{\mathrm{el}}(X)\,\chi_j(X),\, \chi_k(X)\,\rangle_{L^2(\mathbb{R}^{3n})}\,, \qquad X \in \mathbb{R}^{3N}\,, \qquad j,k \in \{1,\ldots,m\}\,.$$

Again by Kato's Theorem, the operator $H^\varepsilon_{\mathrm{BO}}$ is self-adjoint on the domain $H^2(\mathbb{R}^{3N}, \mathbb{C}^m)$.

THEOREM 1 (SPOHN & TEUFEL, [SPTE]) *Let $\sigma_*(X) \subset \sigma(H_{\mathrm{el}}(X))$ be a spectral subset separated from the remainder of the spectrum for all $X \in \mathbb{R}^{3N}$ as it has been described in (6) and (7). Let $\dim \mathrm{Ran}(P_*(\cdot)) = m \in \mathbb{N}$ and $\lambda \in \mathbb{R}$. Then,*

$$\big\|\,\big(e^{-i\,H^\varepsilon_{\mathrm{mol}}\,t/\varepsilon} - U^*\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,t/\varepsilon}\,U\big)\,P_*\,\mathbb{1}_{]-\infty,\lambda]}(H^\varepsilon_{\mathrm{mol}})\,\big\|_{\mathcal{L}(\mathcal{H})} \;\le\; \text{const.}\,\varepsilon\,(1+|t|)$$

for all $t \in \mathbb{R}$ and $\varepsilon > 0$.

Theorem 4 in [SpTe] discusses the effective dynamics on the nucleonic reference space if $\sigma_*(X) = \{E(X)\}$ for all $X \in \Lambda \subset \mathbb{R}^{3N}$, where $E(X)$ is a simple eigenvalue. The following arguments are taken from the proof there.

SKETCH OF PROOF. We have $U^*\,U = \mathrm{Id}_{\mathrm{Ran}(P_*)}$ and $\mathrm{Ran}(P_*) \subset D(H_{\mathrm{el}}) \subset D(H^\varepsilon_{\mathrm{mol}})$. We obtain on the dense set

$$D \;:=\; \Big\{ \int_{\mathbb{R}^{3N}}^{\oplus} \phi(X)\cdot\chi(X)\,dX \;\Big|\; \phi \in H^2(\mathbb{R}^{3N}, \mathbb{C}^m) \Big\} \;\subset\; \mathcal{H}$$

that

$$e^{-i\,H^\varepsilon_{\mathrm{mol}}\,t/\varepsilon} - U^*\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,t/\varepsilon}\,U \;=\; -\,e^{-i\,H^\varepsilon_{\mathrm{mol}}\,t/\varepsilon}\int_0^t \tfrac{d}{ds}\Big(e^{i\,H^\varepsilon_{\mathrm{mol}}\,s/\varepsilon}\,U^*\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,s/\varepsilon}\,U\Big)\,ds$$

and

$$\begin{aligned}
\tfrac{d}{ds}\Big(e^{i\,H^\varepsilon_{\mathrm{mol}}\,s/\varepsilon}\,U^*\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,s/\varepsilon}\,U\Big) \;&=\; \tfrac{i}{\varepsilon}\,e^{i\,H^\varepsilon_{\mathrm{mol}}s/\varepsilon}\,(H^\varepsilon_{\mathrm{mol}}\,U^* - U^*\,H^\varepsilon_{\mathrm{BO}})\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,s/\varepsilon}\,U\\
&=\; \tfrac{i}{\varepsilon}\,e^{i\,H^\varepsilon_{\mathrm{mol}}s/\varepsilon}\,(H^\varepsilon_{\mathrm{mol}} - P_*\,H^\varepsilon_{\mathrm{mol}}\,P_*)\;U^*\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,s/\varepsilon}\,U\\
&+\; \tfrac{i}{\varepsilon}\,e^{i\,H^\varepsilon_{\mathrm{mol}}s/\varepsilon}\,(P_*\,H^\varepsilon_{\mathrm{mol}}\,P_*\,U^* - U^*\,H^\varepsilon_{\mathrm{BO}})\,e^{-i\,H^\varepsilon_{\mathrm{BO}}\,s/\varepsilon}\,U\,.
\end{aligned}$$

The integral from zero to t over the first summand times $P_*\,\mathbb{1}_{]-\infty,\lambda]}(H^\varepsilon_{\mathrm{mol}})$ can be bounded by $\text{const.}\,\varepsilon\,(1+|t|)$ using the same arguments, which yield the bound in (8). Since $\langle\chi_j, \nabla_X\,\chi_j\rangle = 0$, we have for $\phi \in H^2(\mathbb{R}^{3N}, \mathbb{C}^m)$

$$\begin{aligned}
(P_*\,H^\varepsilon_{\mathrm{mol}}\,P_*\,U^*\,\phi)(X) \;&=\; P_*(X)\,(-\tfrac{\varepsilon^2}{2}\Delta_X + H_{\mathrm{el}}(X))\,P_*(X)\,\phi(X)\cdot\chi(X)\\
&=\; (-\tfrac{\varepsilon^2}{2}\Delta_X\,\phi)(X)\cdot\chi(X) + V(X)\phi(X)\cdot\chi(X) - \tfrac{\varepsilon^2}{2}\,\phi(X)\cdot(\Delta_X\,\chi(X))\\
&=\; (U^* H^\varepsilon_{\mathrm{BO}})(X) + \mathcal{O}(\varepsilon^2)\,,
\end{aligned}$$

where the $\mathcal{O}(\varepsilon^2)$ is meant in $L^2(\mathbb{R}^{3n}, \mathbb{C})$. Hence, the second summand is of order ε and contributes another const. $\varepsilon\,(1 + |t|)$ after being integrated from zero to t. $\square$

Let $\phi \in C(\mathbb{R}, L^2(\mathbb{R}^{3N}, \mathbb{C}^m))$ be the solution of the time-dependent m-level system

$$i\,\varepsilon\,\partial_t \phi \;=\; H^{\varepsilon}_{\mathrm{BO}}\,\phi\,, \qquad \phi(0) \;=\; \phi_0 \in L^2(\mathbb{R}^{3N}, \mathbb{C}^m)\,.$$

By Theorem 1,

$$\psi \;=\; \psi(t,x,X) \;=\; \phi(t,X) \cdot \chi(X)(x)$$

is an approximation of order ε to the solution of the full molecular problem

$$i\,\varepsilon\,\partial_t \psi \;=\; H^{\varepsilon}_{\mathrm{mol}}\,\psi\,, \qquad \psi(0,x,X) = \phi_0(X) \cdot \chi(X)(x)\,.$$

Hence, we have just rephrased once more, that the time-dependent Born-Oppenheimer approximation gives effective dynamics on the nucleonic configuration space $\mathbb{R}^{3N}$, which approximate the full dynamics on the molecular configuration space $\mathbb{R}^{3(n+N)}$ with an error of order ε.

2.3 Berry Phase

Since the spectral subspaces $\sigma_*(X)$ are typically only *locally* isolated from the remainder of the electronic spectrum, one would like to prove a local version of Theorem 1. Such a local proof exists for the case

$$\sigma_*(X) \;=\; \{E(X)\} \qquad \text{for all } \; X \in \Lambda \subsetneq \mathbb{R}^{3N}\,,$$

where $E(X)$ is a simple eigenvalue of $H_{\mathrm{el}}(X)$, which is isolated from the remainder of the spectrum for all $X \in \Lambda$, see Theorem 4 in [SpTe]. In general, the subset $\Lambda \subsetneq \mathbb{R}^{3N}$ is not contractible, and the Berry connection

$$A(X) \;:=\; i\,\langle \chi(X), \nabla_X\,\chi(X) \rangle_{L^2(\mathbb{R}^{3n})} \;\neq\; 0$$

cannot be gauged away. Hence, the effective one-band Born-Oppenheimer Hamiltonian takes the form

$$H^{\varepsilon}_{\mathrm{BO}} \;=\; \tfrac{\varepsilon^2}{2}\,\Delta^{A}_{X} + E(X)\,, \tag{10}$$

where

$$\begin{aligned} \tfrac{\varepsilon^2}{2}\,\Delta^{A}_{X} \;&:=\; \tfrac{\varepsilon^2}{2}\,(-\,i\nabla_X - A(X))^2 \\ &=\; -\tfrac{\varepsilon^2}{2}\,\Delta_X \;+\; \tfrac{\varepsilon}{2}\,(i\varepsilon\nabla_X \cdot A(X) + A(X) \cdot i\varepsilon\nabla_X) \;+\; \tfrac{\varepsilon^2}{2}\;A(X) \cdot A(X) \end{aligned}$$

is the Laplacian of the covariant derivative with respect to the Berry connection $A(X)$. Since the connection $A(X)$ is a term of order ε in the covariant Laplacian or, in other words, a subprincipal term of the Born-Oppenheimer Hamiltonian, $A(X)$ does not contribute to the leading order dynamics in the semi-classical limit $\varepsilon \to 0$. Let Γ be a bounded subset of the nucleonic phase space $T^*\mathbb{R}^{3N} = \mathbb{R}^{6N}$ with $\pi_X(\Gamma) \subset \Lambda$, where $\pi_X : \mathbb{R}^{6N} \to \mathbb{R}^{3N}$ denotes the projection onto position space. One fixes a maximal time interval $I_{\mathrm{max}}(\Gamma)$, within which the unitary group $e^{-i H_{BO}^{\varepsilon} t/\varepsilon}$ propagates wave functions with phase space support inside Γ to wave functions with phase space support inside Γ, up to an error of order ε. Then, for all times $t \in I_{max}(\Gamma)$

$$\left\| \left(e^{-i H_{mol}^{\varepsilon} t/\varepsilon} - U^* e^{-i H_{BO}^{\varepsilon} t/\varepsilon} U\right) P_\Gamma \right\|_{\mathcal{L}(\mathcal{H})} \leq \text{const.}\, \varepsilon\,, \tag{11}$$

where P_Γ is an approximate projection, which roughly speaking projects onto functions with phase space support inside Γ. We will become more precise concerning the notion of the phase space support of a wave function later on in Section 5 of Part B. Moreover, in its rigorous formulation, Theorem 4 of [SpTe] requires some additional $\delta > 0$ here and there, which we have suppressed in favour of an explanation of the basic idea. The determination of the time interval $I_{max}(\Gamma)$ requires some rough a priori knowledge about the effective Born-Oppenheimer dynamics $e^{-i H_{BO}^{\varepsilon} t/\varepsilon}$. Hence, it is the bottle-neck for an extension of the local approximation to the case of spectral subspaces associated with several different eigenvalues. For scalar operators like the single band Hamiltonian (10), this a priori information can be drawn from Egorov's Theorem, see Theorem 7 in Part B later on. In the case of matrix-valued operators, however, Egorov type Theorems are only available for systems with eigenvalues of constant multiplicity, see Theorem 3 in [BrNo] or Theorem 3.2 in [BoGl].
We conclude this short intermezzo about the Berry phase by a concrete example. We put the model Hamiltonian

$$H^\varepsilon \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_q \;+\; V(q) \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_q \;+\; \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}$$

in place of the full molecular Hamiltonian H_{mol}^{ε} and study the dynamics associated with one of the spectral subspaces

$$\sigma_\pm(q) \;=\; \{\pm|q|\}\,, \qquad q \in \mathbb{R}^2 \setminus \{(0,0)\}\,.$$

Let $\chi^\pm(q) \in C^\infty(\mathbb{R}^2, \mathbb{C}^2)$ be smooth eigenvectors of $V(q)$ corresponding to the eigenvalues $E^\pm(q) = \pm|q|$. For example, $\chi^\pm(q) = \chi^\pm(r,\varphi)$,

$$\chi^+(r,\varphi) \;=\; e^{i\varphi/2} \begin{pmatrix} \cos(\varphi/2) \\ \sin(\varphi/2) \end{pmatrix}, \qquad \chi^-(r,\varphi) \;=\; e^{i\varphi/2} \begin{pmatrix} -\sin(\varphi/2) \\ \cos(\varphi/2) \end{pmatrix} \tag{12}$$

with $(r,\varphi) \in [0,\infty[\times[0,2\pi[$. We decompose the solution of the full Schrödinger system (1) as

$$\psi(t,q) = \psi^+(t,q)\,\chi^+(q) + \psi^-(t,q)\,\chi^-(q)\,, \qquad (t,q) \in \mathbb{R}\times\mathbb{R}^2\,.$$

Then, we infer from (11) that the scalar components $\psi^\pm(t) \in L^2(\mathbb{R}^2,\mathbb{C})$ approximately satisfy the effective Born-Oppenheimer equations of motion

$$\begin{aligned} i\,\varepsilon\,\partial_t \psi^+(t,q) &= \left(\tfrac{\varepsilon^2}{2}\,\Delta_q^{A^+} + E^+(q)\right)\psi^+(t,q)\,, \\ i\,\varepsilon\,\partial_t \psi^-(t,q) &= \left(\tfrac{\varepsilon^2}{2}\,\Delta_q^{A^-} + E^-(q)\right)\psi^-(t,q)\,, \end{aligned} \tag{13}$$

as long as $\psi(t,q)$ has phase space support *away* from the crossing $q = 0$. Here,

$$\Delta_q^{A^\pm} \;=\; (-i\nabla_q - A^\pm(q))^2\,, \qquad A^\pm(q) \;=\; i\,\langle \chi^\pm(q),\, \nabla_q\,\chi^\pm(q)\rangle_{\mathbb{C}^2}\,.$$

We see, that even away from the crossing the solution $\psi(t,q)$ feels the presence of the crossing as a first order correction to its dynamics.

3 Origin of the Model in Molecular Dynamics

Formulating the effective version of Born-Oppenheimer approximation for Theorem 1, we have seen that if the electronic part of the full molecular Hamiltonian has a pair of eigenvalue surfaces, which are globally isolated from the remainder of the electronic spectrum, then the full molecular problem (9) reduces to a two-band model of the form

$$\begin{aligned} i\,\varepsilon\,\partial_t\psi(t,X) &= -\tfrac{\varepsilon^2}{2}\,\Delta_X\psi(t,X) + \widetilde{V}(X)\,\psi(t,X)\,, \\ \psi(0,X) &= \psi_0(X) \in L^2(\mathbb{R}^{3N},\mathbb{C}^m)\,, \end{aligned}$$

where the semi-classical parameter $\varepsilon = M_{\text{nuc}}^{-1/2}$ is given by the inverse square root of the nucleonic mass. The potential $\widetilde{V}(X)$ is a hermitian $m \times m$-matrix, where $m \in \mathbb{N}$ is the dimension of the electronic subspace, which depends on the degeneracy of the eigenvalue surfaces.

3.1 Derivation of the Model

In Chapter 2 of the monograph [Ha94], G. Hagedorn has analysed the (co-) representations of the symmetry group associated with the electronic Hamiltonian of the full molecular problem. From this analysis he derives a classification of eleven types of eigenvalue crossings of minimal multiplicity. We denote by $E^{\pm}(X)$ the eigenvalues of $\widetilde{V}(X)$ and by

$$\Gamma \;=\; \{X \in \mathbb{R}^{3N} \mid E^+(X) \;=\; E^-(X)\}$$

the crossing manifold.

Theorem 2 (Hagedorn, [Ha94]) *For electron energy level crossings of the minimal multiplicity allowed by the symmetry group of the electronic Hamiltonian, the crossing manifold Γ can be of codimension one, two, three, or five in the nucleonic configuration space,*

$$\operatorname{codim}_{\mathbb{R}^{3N}}(\Gamma) \in \{1,2,3,5\}\,.$$

Codimension two crossings are met for time-reversal invariant systems with an even number of electrons. Time-reversal invariance exludes for example an external magnetic field in the full molecular Hamiltonian, which for the sake of simplicity we did not include in our presentation anyway. For time-reversal invariant systems, the matrix $\widetilde{V}(X)$ is real symmetric,

$$\widetilde{V}(X) \;=\; \operatorname{tr}(\widetilde{V}(X)) + \begin{pmatrix} \alpha(X) & \beta(X) \\ \beta(X) & -\alpha(X) \end{pmatrix} \tag{14}$$

for some $\alpha,\beta \in C_b^\infty(\mathbb{R}^{3N},\mathbb{R})$. The eigenvalues $E^{\pm}(X)$ are given as

$$E^{\pm}(X) \;=\; \operatorname{tr}(\widetilde{V}(X)) \pm \sqrt{\alpha(X)^2 + \beta(X)^2}$$

and cross for $X \in \mathbb{R}^{3N}$ with $\alpha(X) = \beta(X) = 0$. For real symmetric matrices, such a crossing of eigenvalues generically occurs on a codimension two submanifold, and after a change of coordinates we can assume

$$\Gamma \;=\; \{\, X \in \mathbb{R}^{3N} \mid X_1 = X_2 = 0 \,\}.$$

Neglecting the trace, Taylor expansion around the point $X = 0$ provides $\widetilde{V}$ of the form

$$\widetilde{V}(X) \;=\; \begin{pmatrix} \alpha_0 \cdot X & \beta_0 \cdot X \\ \beta_0 \cdot X & -\alpha_0 \cdot X \end{pmatrix} + \mathcal{O}(|X^2|)\,,$$

where the vectors $\alpha_0, \beta_0 \in \mathbb{R}^{3N}$ are linearly independent. An appropriate rotation eliminates all but the first two components of α_0 and β_0 and thus leaves us with linearly independent vectors $a, b \in \mathbb{R}^2$ and

$$V(\widetilde{X}) \;=\; \begin{pmatrix} a \cdot \widetilde{X} & b \cdot \widetilde{X} \\ b \cdot \widetilde{X} & -a \cdot \widetilde{X} \end{pmatrix}, \qquad \widetilde{X} = (X_1, X_2) \in \mathbb{R}^2\,,$$

which is the potential of our model problem if $a = (1,0)^t$ and $b = (0,1)^t$. The reduction process from the matrix $\widetilde{V}(X)$ in (14) to the linear potential $V(\widetilde{X})$ involves nonlinear changes of coordinates, which affect the Laplacian $-\frac{\varepsilon^2}{2}\Delta_X$. Hence, the Schrödinger equation (1) must be considered just as a *model system* designed to capture the generic features of a codimension two crossing in molecular dynamics. More or less the same derivation of the model system (1) can be found in Chapter 2 of G. Hagedorn's monograph [Ha94] or in Appendix A of the lecture notes of F. Bornemann [Bo].

3.2 Examples of Conical Crossings

The plot of the electron energ levels of nitrogen in Figure 2 brings us to expect an abundance of level crossings in molecular dynamics. With respect to codimension two crossings, the chemist L. Cederbaum and coworkers assert that "conical intersections of potential surfaces are in fact ubiquitous", cit. [CFRM]. We mention some prominent examples:

Molecular collisions. The simplest and most studied example for this class of phenomena is the reactive collision $H + H_2 \to H_2 + H$ of the hydrogen atom with the hydrogen molecule, see [Go]. The conical intersection corresponds to the configuration, in which the three nuclei arrange on the edges of an equilateral triangle, and the system forms the transient molecule H_3. Away from the crossing, one nucleus is farther away from the other two, and the system falls into one hydrogen atom and one hydrogen molecule. In experiments, the hydrogen atom is usually replaced by its isotop deuterium D, and one studies the reaction $D + H_2 \to DH + H$, which has distinguishable reactants, see also [TuPr].

Ultrafast electronic relaxation. W. Domcke and coworkers [SDK] have identified a conical intersection of the lowest two excited singlet states of the organic molecule pyrazine $C_4H_4N_2$, which triggers the internal conversion from the S_2 to the S_1 state on a femtosecond time scale. One assumes an initial preparation of the S_2 state by a short laser pulse, that is an excitation of the molecule by ultraviolet light. Within

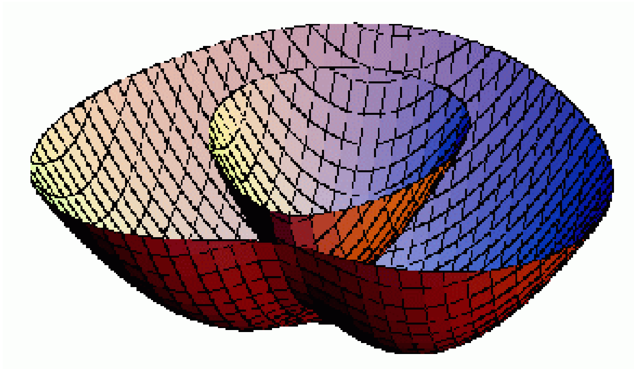


Figure 3: Model for the intersecting S_1 and S_2 electronic state of the molecule pyrazine. The plot is taken from the web page of the John von Neumann Institut for Computing (NIC) at Jülich, Germany.

a few hundred femtoseconds the population probability of the S_2 state exhibits an initial decay followed by quasi-periodic damped recurrences of the population, see Section II.C in [StTh].

Photoreactions in proteins. The first step in vision, the photoisomerization of retinal in rhodopsin is modelled by a two-state system having a conical intersection of its energy surfaces [HaSt]. Rhodopsin is the light-absorbing pigment of the rods, which are the light receptors inside the eye's retina generating colorless vision. Rhodopsin consists of a protein called opsin coupled to a derivative of vitamin A called retinal. When light is absorbed, retinal switches from the stable cis-configuration to the unstable trans-configuration. Figure 4 shows these two configurations. In the 11-cis configuration the hydrogen atoms attached to the number eleven and twelve carbon atoms point towards the same direction producing a kink in the molecule. In the all-trans configuration the number twelve hydrogen atom has flipped down, and the molecule is straightened out. This switch triggers a change in the pattern of impulses sent along the optic nerve. The isomerization occurs within a couple of hundred femtoseconds. As a reaction of high speed and efficiency, this isomerization is only observed for retinal in rhodopsin, but not for retinal in solution.

4 The Results of Hagedorn

The mathematical results on the propagation through conical crossings can be organized into two groups: the semi-classical propagation of coherent states and the approaches within the framework of microlocal analysis. Since we provide the basic concepts of pseudodifferential calculus in detail later on, we postpone a discussion of the microlocal results to Section 12.5 in Part C, when the precise vocabulary is available. Chapter 6 of G. Hagedorn's monograph [Ha94] contains the result on propagation of semi-classical wave packets through

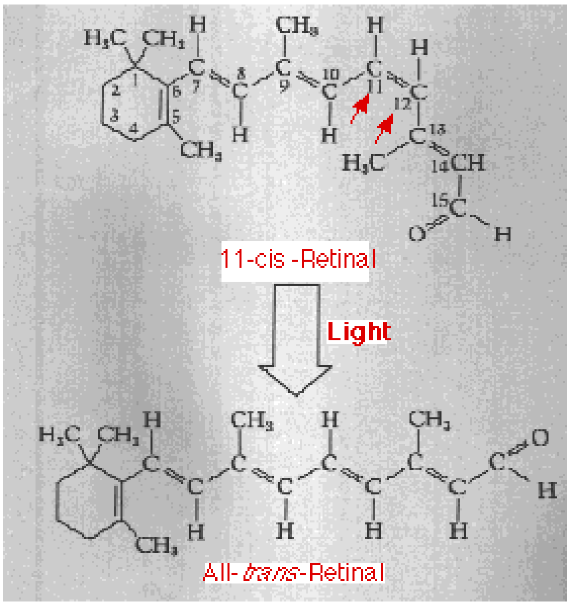


Figure 4: The 11-cis configuration of retinal and its all-trans isomer. The cis-trans isomerization of retinal in rhodopsin triggers a change in the pattern of impulses sent along the optic nerve, the first step of vision. The picture is taken from the webpage of J. Kimball's online biology textbook.

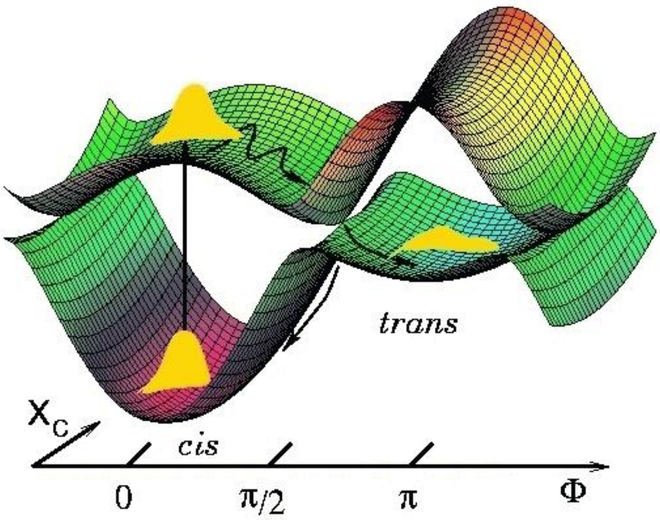


Figure 5: Energy surfaces of a two-state model of two degrees of freedom for the cis-trans isomerization of retinal in rhodopsin. The wave-packet initially associated with the cis configuration is vertically excited and bifurcates when running down the upper surface. The plot is taken from [HaSt].

codimension two crossings. He considers the time-dependent Schrödinger equation

$$i\varepsilon\partial_t\psi \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_X\,\psi + H_{\mathrm{el}}(X)\,\psi\,, \qquad \psi(-T) \;=\; \psi_{-T} \;\in\; L^2(\mathbb{R}^{3(N+n)},\mathbb{C})$$

on a bounded time interval $[-T,T]$ for an electronic Hamiltonian $H_{\mathrm{el}}(X)$ with

$$(H_{\mathrm{el}}(\cdot)-i)^{-1} \in C^k(\mathbb{R}^{3N},\mathcal{L}(L^2(\mathbb{R}^{3n},\mathbb{C})))\,, \qquad k \geq 3\,.$$

$H_{\mathrm{el}}(X)$ has two simple eigenvalues $E^+(X)$ and $E^-(X)$, which depend continuously on the nucleonic configuration $X \in \mathbb{R}^{3N}$ and cross on a codimension two manifold Γ of the nucleonic configuration space $\mathbb{R}^{3N}$. Γ is assumed to contain the origin. The time interval $[-T,T]$ is chosen, such that all the ordinary differential equations to be introduced later on have well-defined unique solutions. By Proposition 3.1 in [Ha94], there are eigenfunctions $\chi^\pm(X) \in L^2(\mathbb{R}^{3n},\mathbb{C})$ of $H_{\mathrm{el}}(X)$ for the eigenvalue $E^\pm(X)$ such that away from the crossing manifold Γ

$$\left\langle \chi^\pm(X),\, \eta\cdot\nabla_X\,\chi^\pm(X)\right\rangle_{L^2(\mathbb{R}^{3n})} \;=\; 0$$

for all $\eta \in \mathbb{R}^{3N}$. The initial data are of the form

$$\psi_{-T}(x,X) \;=\; \phi_l(X)\,\chi^-(X)(x)\,, \tag{15}$$

where $\phi_l(X)$ is a semi-classical wave packet. Roughly speaking, a semi-classical wave packet is the product of a generalized Hermite type polynomial and a Gaussian wave packet. More precisely,

$$\begin{aligned} \phi_l(X) \;&=\; \phi_l(A,B,\varepsilon,a,\eta;X) \qquad (16)\\ &=\; C^\varepsilon_{l,A}\;\mathcal{H}_{l,A}\big((\varepsilon|A|)^{-1}(X-a)\big)\,\exp\big(-\tfrac{1}{2\varepsilon}\langle (X-a),BA^{-1}(X-a)\rangle + \tfrac{i}{\varepsilon}\,\langle \eta, X-a\rangle\big)\,, \end{aligned}$$

where $l \in \mathbb{N}_0^{3N}$ is a multi-index, $A,B \in GL(3N,\mathbb{C})$ invertible complex $3N\times 3N$-matrices, $a,\eta \in \mathbb{R}^{3N}$ vectors, and $\langle\cdot,\cdot\rangle$ the Euclidian inner product in $\mathbb{C}^{3N}$. The matrices A and B are such that

$$BA^{-1} \quad \text{is symmetric}\,, \qquad \mathrm{Re}(BA^{-1}) = AA^* > 0\,. \tag{17}$$

The normalizing constant $C^\varepsilon_{l,A} \in \mathbb{C}$ is given as

$$C^\varepsilon_{l,A} \;=\; 2^{-|l|/2}\,(l\,!)^{-1/2}\,(\varepsilon\pi)^{-3N/4}\,(\det A)^{-1}\,,$$

while the polynomial $\mathcal{H}_{l,A}$ is constructed as follows. For $m \geq 2$ and arbitrary vectors $v_1,\dots,v_m \in \mathbb{C}^{3N}\setminus\{0\}$ one recursively defines the mth generalized Hermite polynomial $\widetilde{\mathcal{H}}_m(v_1,\dots,v_m;X)$ by

$$\widetilde{\mathcal{H}}_0(X) \;=\; 1\,, \quad \widetilde{\mathcal{H}}_1(v_1;X) \;=\; 2\,\langle v_1,X\rangle$$

and

$$\begin{aligned} \widetilde{\mathcal{H}}_m(v_1,\dots,v_m;X) \;&=\; 2\,\langle v_m,X\rangle\,\widetilde{\mathcal{H}}_{m-1}(v_1,\dots,v_{m-1};X)\\ &-\; 2\sum_{j=1}^{m-1}\langle v_m,\bar{v}_j\rangle\;\widetilde{\mathcal{H}}_{m-2}(v_1,\dots,v_{j-1},v_{j+1},\dots,v_{m-1};X)\,. \end{aligned}$$

The unitary matrix of the polar decomposition of A is denoted by U_A, that is $A = |A|\,U_A = (AA^*)^{1/2}\,U_A$, and one sets

$$\mathcal{H}_{l,A}(X) \;=\; \widetilde{\mathcal{H}}_{|l|}\,(U_A e_1,\ldots,U_A e_1,U_A e_2,\ldots,U_A e_2,\ldots\ldots,U_A e_{3N},\ldots,U_A e_{3N};X)\;,$$

where the entry $U_A e_j$ is repeated for l_j times. For fixed A, B, ε, a, and η the wave packets ϕ_l, $l \in \mathbb{N}_0^{3N}$, form an orthonormal basis of $L^2(\mathbb{R}^{3N},\mathbb{C})$, see Lemma 2.1 of [Ha85]. Moreover, they behave favourably with respect to the normalized ε-scaled Fourier transform

$$(\mathcal{F}_\varepsilon\,\psi)(\Xi) \;:=\; (2\pi\varepsilon)^{-3N/2}\int_{\mathbb{R}^{3N}} e^{-\,i\,X\cdot\,\Xi\,/\,\varepsilon}\,\psi(X)\,dX\,.$$

One has

$$(\mathcal{F}_\varepsilon\,\phi_l(A,B,\varepsilon,a,\eta,\cdot))(\Xi) \;=\; (-i)^{|l|}\;e^{-i\,\langle\eta,a\rangle/\varepsilon}\;\phi_l(B,A,\varepsilon,\eta,-a,\Xi)\,,$$

see Lemma 2.2 in [Ha85]. We will need the Hamiltonian systems associated with the eigenvalues $E^\pm$

$$\tfrac{d}{dt}\,a^\pm(t) \;=\; \eta^\pm(t)\,, \qquad \tfrac{d}{dt}\,\eta^\pm(t) \;=\; -\nabla_X\,E^\pm(a^\pm(t))\,. \tag{18}$$

Lemma 6.1 in [Ha94] guarantees existence and uniqueness of solutions $(a^\pm(\cdot),\eta^\pm(\cdot))$ satisfying

$$(a^\pm(0),\eta^\pm(0)) \;=\; (0,\eta_0)$$

with $\eta_0 \neq 0$ not tangent to Γ at the origin. The wave packet $\phi_l(X)$ building the initial datum (15) is chosen as

$$\phi_l(X) \;=\; \phi_l(A,B,\varepsilon,a^-(-T),\eta^-(-T);X)\,, \tag{19}$$

where the matrices A, B satisfy condition (17). Hence, the initial wave packet is prepared such that its center hits the origin at time $t = 0$. For an approximate solution with the correct phase one further needs the classical action integrals of the Hamiltonian system (18)

$$\begin{aligned} S^-(t) \;&=\; \int_{-T}^{t}\big(\tfrac{1}{2}\,\eta^-(s)^2 - E^-(a^-(s))\big)\,ds\;,\\ S^+(t) \;&=\; \int_{0}^{t}\big(\tfrac{1}{2}\,\eta^+(s)^2 - E^+(a^+(s))\big)\,ds \;+\; S^-(0)\,. \end{aligned}$$

Theorem 3 (Hagedorn, [Ha94]) *Let* $\psi^\varepsilon(t) \in C(\mathbb{R},L^2(\mathbb{R}^{3(N+n)},\mathbb{C}))$ *be the solution of the Schrödinger equation*

$$i\varepsilon\partial_t\psi^\varepsilon \;=\; -\tfrac{\varepsilon^2}{2}\,\Delta_X\,\psi^\varepsilon + H_{el}(X)\,\psi^\varepsilon\,, \qquad \psi^\varepsilon(-T) \;=\; \psi^\varepsilon_{-T}$$

with initial datum ψ^ε_{-T} *of the form described in (15) and (19).*

Then, for times "before the crossing event", that is for all times $t \in [-T,-T_1]$ *with* $0 < T_1 < T$, *there are matrices* $A^-(t)$ *and* $B^-(t)$ *satisfying condition (17) such that the solution* $\psi^\varepsilon(t)$ *can be described as*

$$\psi^\varepsilon(t,x,X) \;=\; \chi^-(X)(x)\;e^{i\,S^-(t)/\varepsilon}\;\phi_l(A^-(t),B^-(t),\varepsilon,a^-(t),\eta^-(t);X) \;+\; \mathcal{O}(\sqrt{\varepsilon})\,.$$

For times "after the crossing event", that is for times $t \in [T_1, T]$ *there are matrices* $A^{\pm}(t)$ *and* $B^{\pm}(t)$ *satisfying condition (17), functions* $d_m^{\pm} : \mathbb{R} \times \mathbb{R}^{3N} \to \mathbb{C}$*, and a positive number* $\alpha > 0$ *such that* $\psi^{\varepsilon}(t)$ *is approximated as*

$$\begin{aligned}\psi^{\varepsilon}(t,x,X) &= \chi^{-}(X)(x)\, e^{i\,S^{-}(t)/\varepsilon} \sum_{m} d_m^{-}(t,X)\, \phi_m(A^{-}(t), B^{-}(t), \varepsilon, a^{-}(t), \eta^{-}(t); X) \\ &+ \chi^{+}(X)(x)\, e^{i\,S^{+}(t)/\varepsilon} \sum_{|m| \le |l|} d_m^{+}(t,X)\, \phi_m(A^{+}(t), B^{+}(t), \varepsilon, a^{+}(t), \eta^{+}(t); X) \\ &+ \mathcal{O}(\varepsilon^{\alpha})\,.\end{aligned}$$

The previous Theorem 3 is a light version of Theorem 6.3 in [Ha94]. There, even the explicit construction of the matrices $A^{\pm}(t)$ and $B^{\pm}(t)$ is given, which control position and momentum uncertainty of the wave packets. For the proof, an incoming outer solution is matched to an inner solution, which is valid for times $t \sim 0$ near the "crossing event".

Remark 2 For times after the crossing event, the approximate solution associated with the initially occupied level is an *infinite* superposition of semi-classical wave packets. In the plots of Figure 1, initially there is one Gaussian on the upper level. The crossing sucks the Gaussian's center part onto the lower level and leaves two demolished bumps on the upper level. Y. Colin de Verdiére [CdV] has desribed this situation as "the dromedary becomes a bactrian". The Landau-Zener formula in (41) will explain this phenomen less zoologically. $\diamondsuit$

Part B

Semi-Classical Calculus

5 Wigner Functions

Discussing the local version of time-dependent Born-Oppenheimer approximation, we have used the notion of the phase space support of a wave function. It is our aim now to recall, in which way the Wigner function gives a precise meaning to this concept.

Definition 1 (Wigner, [Wi]) Let $\psi \in \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$ be a Schwartz function with values in $\mathbb{C}^m$, and let $\varepsilon > 0$. Then we define the Wigner function $W^\varepsilon(\psi) \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^m))$ by

$$W^\varepsilon(\psi)(q,p) \;=\; (2\pi)^{-n} \int_{\mathbb{R}^n} e^{i\,y\cdot p}\, \psi(q - \tfrac{\varepsilon}{2}\,y) \otimes \overline{\psi}(q + \tfrac{\varepsilon}{2}\,y)\, dy$$

with $(q,p) \in T^*\mathbb{R}^n = \mathbb{R}^{2n}$.

That the Wigner function takes values in the space of hermitian $m \times m$-matrices is immediate from its definition. Verifying that the Wigner function of a Schwartz function is indeed a Schwartz function on phase space, one denotes $\phi^\varepsilon(q,y) := \psi(q - \frac{\varepsilon}{2}y) \otimes \overline{\psi}(q + \frac{\varepsilon}{2}y)$ and observes

$$W^\varepsilon(\psi)(q,p) \;=\; (\mathcal{F}_2^{-1}\phi^\varepsilon)(q,p)\,,$$

where $\mathcal{F}_2^{-1}$ is the inverse Fourier transform with respect to the second argument. Moreover, by this observation Wigner transformation extends from a continuous linear mapping on Schwartz functions to a mapping on temperate distributions

$$W^\varepsilon :\; \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}'(\mathbb{R}^{2n}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^m))$$

and square-integrable functions

$$W^\varepsilon :\; L^2(\mathbb{R}^n, \mathbb{C}^m) \;\to\; L^2(\mathbb{R}^{2n}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^m)) \cap C_0(\mathbb{R}^{2n}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^m))\,,$$

see Chapter 1.8 in [Fo]. As an example, one may compute the Wigner function of a scalar-valued Gaussian wave packet, which is centered around position $q_0 \in \mathbb{R}^n$ and momentum $p_0 \in \mathbb{R}^n$,

$$g^\varepsilon(q) \;=\; 2^{-1/2}\,(\varepsilon\pi)^{-n/4}\, \exp(\,-\tfrac{1}{2\varepsilon}\,|q - q_0|^2 + \tfrac{i}{\varepsilon}\,p_0 \cdot (q - q_0)\,)\,.$$

One obtains

$$W^\varepsilon(g^\varepsilon)(q,p) \;=\; 2^{-(2n+1)}\,(\varepsilon\pi)^{-n}\, \exp(\,-\tfrac{1}{\varepsilon}\,(|q - q_0|^2 + |p - p_0|^2)\,)\,. \tag{20}$$

Remark 3 Let $\psi, \phi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$. If $W^\varepsilon(\psi) = W^\varepsilon(\phi)$, then Fourier inversion gives $\psi(u) \otimes \overline{\psi}(v) = \phi(u) \otimes \overline{\phi}(v)$ for almost all $u, v \in \mathbb{R}^n$ and $|\psi_j(u)|^2 = |\phi_j(u)|^2$, $j = 1, \ldots, m$, for almost all $u \in \mathbb{R}^n$. Hence, the Wigner function uniquely represents a wave function up to a global phase factor $c \in \mathbb{C}$ with $|c| = 1$. In formulae,

$$W^\varepsilon(\psi) \;=\; W^\varepsilon(\phi) \quad\Longleftrightarrow\quad \psi \;=\; c\,\phi\,.$$

Of course, the statement remains true for temperate distributions $\psi, \phi \in \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m)$. $\diamondsuit$

From the preceding discussion we see, that the Wigner function is a suitable candidate for the definition of a wave function's phase space support. The notion that $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$ has phase space support inside some set $\Gamma \subset \mathbb{R}^{2n}$ up to order ε could be expressed as

$$\int_{\mathbb{R}^{2n}} W^\varepsilon(\psi)(q,p)\, a(q,p)\, dq\, dp \;=\; \mathcal{O}(\varepsilon)$$

for all $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}_{\mathsf{sa}}(\mathbb{C}^m))$ with $\mathrm{supp}(a) \subset (\mathbb{R}^{2n} \setminus \Gamma)$. Here, we have treated the Wigner function as a temperate distribution. That $W^\varepsilon(\psi)$ is indeed a continuous linear functional on $\mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ will be become clear later on, when we recall the Theorem of Calderón-Vaillancourt. Before taking this distributional point of view, we return to the Wigner function as an honest continuous function on phase space. We have the following information concerning its support.

Lemma 3 (Support) *Let $\pi_q : \mathbb{R}^{2n} \to \mathbb{R}^n$, $(q,p) \mapsto q$ and $\pi_p : \mathbb{R}^{2n} \to \mathbb{R}^n$, $(q,p) \mapsto p$ be the projections onto position and momentum space. Let $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$ and $\varepsilon > 0$. Then,*

$$\pi_q(\mathrm{supp}(W^\varepsilon(\psi))) \subset \overline{\mathrm{hull}(\mathrm{supp}(\psi))}\,, \qquad \pi_p(\mathrm{supp}(W^\varepsilon(\psi))) \subset \overline{\mathrm{hull}(\mathrm{supp}(\mathcal{F}_\varepsilon\psi))}\,,$$

where $\mathrm{hull}(M)$ *denotes the convex hull of a set $M \subset \mathbb{R}^n$ and $\mathcal{F}_\varepsilon\psi$ the ε-scaled Fourier transform*

$$(\mathcal{F}_\varepsilon\,\psi)(p) \;:=\; (\mathcal{F}\,\psi)(\tfrac{p}{\varepsilon}) \;=\; \int_{\mathbb{R}^{3N}} e^{-i\,q\cdot p\,/\varepsilon}\,\psi(q)\,dq\,.$$

We note, that this version of the Fourier transform is not normalized. However, we have adopted this unnormalized form here and in the following, since it seems to be the established one in a partial differential equations' context, see [Ho1].

Proof. Let $(q,p) \in \mathbb{R}^{2n}$. If $W^\varepsilon(\psi)(q,p) \neq 0$, then there exist $y \in \mathbb{R}^n$ such that $\{q \pm \frac{\varepsilon}{2}\,y\} \subset \mathrm{supp}(\psi)$. Hence, q lies in the middle of a line connecting two points in the support of ψ, that is, $q \in \mathrm{hull}(\mathrm{supp}(\psi))$. Proving the second claim, we calculate for Schwartz functions $\psi \in \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$

$$\begin{aligned}
W^\varepsilon(\psi)(q,p) &= (2\pi)^{-n} \int_{\mathbb{R}^n} e^{i\,y\cdot p}\,\psi(q - \tfrac{\varepsilon}{2}\,y) \otimes \overline{\psi}(q + \tfrac{\varepsilon}{2}\,y)\,dy \\
&= (2\pi)^{-n}\,(2\varepsilon\pi)^{-2n} \int_{\mathbb{R}^{3n}} e^{i\,y\cdot p}\, e^{i\,v\cdot(q - \frac{\varepsilon}{2}y)/\varepsilon}\, e^{-i\,w\cdot(q+\frac{\varepsilon}{2}y)/\varepsilon} \ldots \\
&\qquad\qquad \ldots\;(\mathcal{F}_\varepsilon\psi)(v) \otimes \overline{(\mathcal{F}_\varepsilon\psi)}(w)\,dv\,dw\,dy \\
&= (2\pi)^{-n}\,(2\varepsilon\pi)^{-2n} \int_{\mathbb{R}^{3n}} e^{i\,y\cdot(p - y_1)}\, e^{2\,i\,y_2\cdot q/\varepsilon} \ldots \\
&\qquad\qquad \ldots\;(\mathcal{F}_\varepsilon\psi)(y_1 + y_2) \otimes \overline{(\mathcal{F}_\varepsilon\psi)}(y_1 - y_2)\,dy_1\,dy_2\,dy \\
&= (2\varepsilon\pi)^{-2n} \int_{\mathbb{R}^n} e^{2\,i\,y_2\cdot q/\varepsilon}\,(\mathcal{F}_\varepsilon\psi)(p + y_2) \otimes \overline{(\mathcal{F}_\varepsilon\psi)}(p - y_2)\,dy_2 \\
&= (2\pi)^{-n}\,(\varepsilon\pi)^{-n} \int_{\mathbb{R}^n} e^{-i\,y\cdot q}\,(\mathcal{F}_\varepsilon\psi)(p - \tfrac{\varepsilon}{2}\,y) \otimes \overline{(\mathcal{F}_\varepsilon\psi)}(p + \tfrac{\varepsilon}{2}\,y)\,dy \\
&= (\varepsilon\pi)^{-n}\,W^\varepsilon(\mathcal{F}_\varepsilon\psi)(p, -q)\,.
\end{aligned}$$

By the boundedness of Wigner transformation we also have

$$W^\varepsilon(\psi)(q,p) \;=\; (\varepsilon\pi)^{-n}\, W^\varepsilon(\mathcal{F}_\varepsilon\psi)(p,-q)$$

for square-integrable $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$. Therefore, the second claim is proved by the same arguments as the first one. □

We have seen that the Wigner function of a Gaussian wave packet remains Gaussian. However, there is more to be said concerning the relation of Wigner functions and Gaussians.

THEOREM 4 (HUDSON, [HUD]) *Let* $0 \neq \psi \in L^2(\mathbb{R}^n, \mathbb{C})$ *and* $\varepsilon = 1$. *Then,*

$$W^\varepsilon(\psi) \;\geq\; 0 \qquad \Longleftrightarrow \qquad \psi(q) \;=\; \exp(-q\cdot Aq + b\cdot q + c), \quad q \in \mathbb{R}^n,$$

where $A \in GL(n,\mathbb{C})$, $b \in \mathbb{C}^n$, $c \in \mathbb{C}$, *and* $\operatorname{Re} A$ *positive definite.*

Convincing ourselves of the general non-positivity of Wigner functions in a more elementary way, we might just evaluate the Wigner function of an odd function in the origin. Indeed, for $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$ with $\psi(\cdot) = -\psi(-\,\cdot)$ we immediately calculate

$$\operatorname{tr}(W^\varepsilon(\psi)(0,0)) \;=\; -\,(\varepsilon\pi)^{-n}\,\|\psi\|^2_{L^2}\,.$$

Due to its non-positivity, the trace of a Wigner function is *not a probability density* on phase space. However, this is the only missing property for being a phase space density. For $\psi \in \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$ the marginal distributions of $W^\varepsilon(\psi)$ are

$$\begin{aligned} \int_{\mathbb{R}^n} \operatorname{tr}(W^\varepsilon(\psi)(q,p))\, dq \;&=\; (2\pi\varepsilon)^{-n}\,\left|\hat{\psi}\left(\tfrac{p}{\varepsilon}\right)\right|^2, \\ \int_{\mathbb{R}^n} \operatorname{tr}(W^\varepsilon(\psi)(q,p))\, dp \;&=\; |\psi(q)|^2, \end{aligned} \tag{21}$$

and the total mass is then

$$\int_{\mathbb{R}^{2n}} \operatorname{tr}(W^\varepsilon(\psi)(q,p))\, dq\, dp \;=\; \|\psi\|^2_{L^2}\,. \tag{22}$$

The analytic power of Wigner functions stems from its direct relation to expectation values of Weyl quantized operators. Hence, we recapitulate some important basic properties of the Weyl correspondence.

6 WEYL CORRESPONDENCE

Quantization provides a correspondence between classical and quantum-mechanical observables. Semi-classical quantization maps functions on phase space, the so-called symbols, to semi-classically scaled linear operators in $L^2(\mathbb{R}^n, \mathbb{C}^m)$. Such a correspondence

$$\mathcal{Q}:\ \left\{\text{functions} : \mathbb{R}^{2n} \to \mathcal{L}(\mathbb{C}^m)\right\} \;\to\; \left\{\text{linear operators in } L^2(\mathbb{R}^n, \mathbb{C}^m)\right\}$$

shall at least satisfy the following two properties:

1. (a) The projection on the jth q-coordinate, $a : (q,p) \mapsto q_j \,\mathrm{Id}$, corresponds to multiplication with q_j, that is $(\mathcal{Q}a)(\psi)(q) = q_j\,\psi(q)$.
   (b) The projection on the jth p-coordiante, $a : (q,p) \mapsto p_j \,\mathrm{Id}$, corresponds to partial differentiation, that is $(\mathcal{Q}a)(\psi)(q) = -i\varepsilon\partial_j\,\psi(q)$.
   (c) Constant symbols, $a : (q,p) \mapsto c\,\mathrm{Id}$, correspond to multiplication with the constant, that is $(\mathcal{Q}a)(\psi)(q) = c\psi(q)$.
2. The correspondence is linear, that is $\mathcal{Q}(a_1 + a_2) = \mathcal{Q}a_1 + \mathcal{Q}a_2$ and $\mathcal{Q}(ca) = c\,\mathcal{Q}a$ for $c \in \mathbb{C}$.

There exist uncountably many ways of quantizing different classes of symbols. The approach taken by Weyl, however, is the most natural in the context of quantum mechanics.

Definition 2 (Weyl, 1930) Let $a \in L^2(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ and $\varepsilon > 0$. Then we denote by $a(q, -i\varepsilon\nabla_q) \in \mathcal{L}(L^2(\mathbb{R}^n, \mathbb{C}^m))$,

$$a(q, -i\varepsilon\nabla_q)\,\psi(q) \;=\; (2\pi)^{-n}\int_{\mathbb{R}^{2n}} a\left(\tfrac{1}{2}(q+y), \varepsilon p\right)\, e^{i(q-y)\cdot p}\,\psi(y)\,dy\,dp,$$

the corresponding *Weyl quantized operator.*

By means of the ε-scaled inverse Fourier transform with respect to the second argument

$$(\mathcal{F}_{\varepsilon,2}^{-1}\,a)(y,q) \;=\; (2\varepsilon\pi)^{-n}\int_{\mathbb{R}^n} a(y,p)\,e^{i\,q\cdot p/\varepsilon}\,dp\,,$$

we rewrite the preceding definition as

$$a(q, -i\varepsilon\nabla_q)\,\psi(q) \;=\; \int_{\mathbb{R}^n} (\mathcal{F}_{\varepsilon,2}^{-1}\,a)\left(\tfrac{1}{2}(q+y), q-y\right)\,\psi(y)\,dy,$$

and observe, that the defined Weyl operator is a Hilbert-Schmidt operator with kernel

$$K_a^\varepsilon(q,y) \;=\; (\mathcal{F}_{\varepsilon,2}^{-1}\,a)\left(\tfrac{1}{2}(q+y), q-y\right), \qquad q,y \in \mathbb{R}^n\,.$$

Consequently, we have

$$\|a(q,-i\varepsilon\nabla_q)\|_{\mathcal{L}(L^2(\mathbb{R}^n))} \;\le\; \|a(q,-i\varepsilon\nabla_q)\|_{\mathrm{HS}} \;=\; \varepsilon^n\,\|a\|_{L^2(\mathbb{R}^{2n})}\,.$$

Using the Fourier inversion Theorem, we calculate for symbols $a \in L^2(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ and wave functions $\psi \in L^2(R^n, \mathbb{C}^m)$

$$\begin{aligned} a(q,p) = a(q) \quad &\Rightarrow \quad a(q,-i\varepsilon\nabla_q)\,\psi(q) \;=\; a(q)\,\psi(q)\,,\\ a(q,p) = a(p) \quad &\Rightarrow \quad a(q,-i\varepsilon\nabla_q)\,\psi(q) \;=\; \mathcal{F}_\varepsilon^{-1}(a\,(\mathcal{F}_\varepsilon\,\psi))(q)\,, \end{aligned}$$

where $\mathcal{F}_\varepsilon$ and $\mathcal{F}_\varepsilon^{-1}$ are the ε-scaled Fourier and inverse Fourier transform,

$$(\mathcal{F}_\varepsilon\psi)(p) \;=\; \int_{\mathbb{R}^n} e^{-i\,q\cdot p/\varepsilon}\,\psi(q)\,dq\,, \qquad (\mathcal{F}_\varepsilon^{-1}\psi)(q) \;=\; (2\varepsilon\pi)^{-n}\int_{\mathbb{R}^n} e^{i\,q\cdot p/\varepsilon}\,\psi(p)\,dp\,.$$

An explixcit calculation also reveals the fundamental relationship between expectation values with respect to Weyl quantized observables and Wigner functions.

LEMMA 4 *Let* $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ *and* $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$. *Then,*

$$\langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^n)} \;=\; \int_{\mathbb{R}^{2n}} \mathrm{tr}\left(a(q,p)\, W^\varepsilon(\psi)(q,p)\right)\, dq\, dp\,.$$

PROOF.

$$\begin{aligned}
&\int_{\mathbb{R}^{2n}} \mathrm{tr}\left(a(q,p)\, W^\varepsilon(\psi)(q,p)\right)\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} \overline{\psi}(q + \tfrac{\varepsilon}{2}\, y) \cdot a(q,p)\, \psi(q - \tfrac{\varepsilon}{2}\, y)\; e^{i\, y \cdot p}\; dy\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} \overline{\psi}(q) \cdot a\big(q - \tfrac{\varepsilon}{2}\, y, p\big)\, \psi(q - \varepsilon y)\; e^{i\, y \cdot p}\; dy\, dq\, dp \;= \\
&\quad (2\varepsilon\pi)^{-n} \int_{\mathbb{R}^{3n}} \overline{\psi}(q) \cdot a\big(\tfrac{1}{2}\,(q+y), p\big)\, \psi(y)\; e^{i\,(q-y)\cdot p/\varepsilon}\; dy\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} \overline{\psi}(q) \cdot a\big(\tfrac{1}{2}\,(q+y), \varepsilon p\big)\, \psi(y)\; e^{i\,(q-y)\cdot p}\; dy\, dq\, dp \;=\; \langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2}
\end{aligned}$$

□

However, our restrictive choice of square-integrable symbols catches neither the projections nor the constant functions. Thus, we extend the admissible symbol class to the space of temperate distributions $\mathcal{S}'(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ and restrict the quantized operator's domain to the space of Schwartz functions $\mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$. Therefore, Definition 2 is still well-posed, if we make the following modification:

$$a(q, -i\varepsilon\nabla_q) :\; \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m) \quad \text{for} \quad a \in \mathcal{S}'(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))\,.$$

By the Schwartz kernel theorem, Theorem 5.2.1 in [Ho1] or Theorem 51.7 in [Tr], the such defined $a(q, -i\varepsilon\nabla_q)$ is a continuous linear mapping from $\mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$ to $\mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m)$. Moreover,

$$\int_{\mathbb{R}^n} \overline{\psi(q)} \cdot a(q, -i\varepsilon\nabla_q)\phi(q)\, dq \;=\; \int_{\mathbb{R}^n} \overline{a^*(q, -i\varepsilon\nabla_q)\psi(q)} \cdot \phi(q)\, dq$$

for $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ and $\psi, \phi \in \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$, see Proposition 2.6 in [Fo]. This means that the adjoint of a Weyl quantized operator is the Weyl quantization of the adjoint symbol,

$$a(q, -i\varepsilon\nabla_q)^* \;=\; a^*(q, -i\varepsilon\nabla_q)\,.$$

The previous move to distributions, which elegantly allows the quantization of very general symbols, can also be reversed. Quantizing symbols, which are Schwartz functions on phase space, one can extend the operator's domain to temperate distributions,

$$a(q, -i\varepsilon\nabla_q) :\; \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m) \quad \text{for} \quad a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))\,.$$

REMARK 4 Let $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$. Then, the corresponding Weyl quantized operator $a(q, -i\varepsilon\nabla_q)$ is *regularizing*. That is,

$$a(q, -i\varepsilon\nabla_q) \;\in\; \mathcal{L}(\mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m), \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m))\,,$$

see Remark 2.5.6 in [Ma] or the proof of Proposition II-56 in [Ro]. ◊

For the quantization of symbols in the class

$$S_0^0(1) \;=\; C_b^\infty(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$$

of smooth functions, which are bounded together with their derivatives, we reenter the framework of L^2-theory. Constant symbols are still on bord, and we have the following important result at our disposal.

Theorem 5 (Calderón & Vaillancourt, 1971) *Let* $a \in S_0^0(1)$ *and* $\varepsilon \in]0,1]$. *Then,* $a(q, -i\varepsilon\nabla_q) \in \mathcal{L}(L^2(\mathbb{R}^n, \mathbb{C}^m))$*, and there is a positive constant* $C_{CV} > 0$ *independent of* a *and* ε *with*

$$\|a(q, -i\varepsilon\nabla_q)\|_{\mathcal{L}(L^2(\mathbb{R}^n))} \quad \leq \quad C_{CV} \sum_{|\alpha| \leq 2n+1} \|\partial^\alpha a\|_\infty \,.$$

The original version of the Calderón-Vaillancourt Theorem applied to scalar-valued symbols $a \in C_b^{2n+1}(\mathbb{R}^{2n}, \mathbb{C})$ and the case $\varepsilon = 1$. However, the standard proof involving the Cotlar-Stein Lemma almost literally extends to the general case with matrix-valued symbols and semi-classical scaling, see Theorem 7.11 in [DiSj] or Theorem 2.8.1 in [Ma]. If we set

$$c_{2n}(a) \;:=\; C_{CV} \sum_{|\alpha| \leq 2n+1} \|\partial^\alpha a\|_\infty$$

for $a \in S_0^0(1)$, then we have for $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$

$$|\, \langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^n)} \,| \leq \; c_{2n}(a)\, \|\psi\|^2_{L^2(\mathbb{R}^n)} \,.$$

If one equips $S_0^0(1)$ with the topology induced by the family of semi-norms $(\|\partial^\alpha \cdot\|_\infty)_{\alpha \in \mathbb{N}_0^n}$, then $S_0^0(1)$ is a Fréchet space. Hence, by the previous bound, the mapping

$$S_0^0(1) \to \mathbb{C}\,, \quad a \mapsto \langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle$$

is a continuous linear functional on $S_0^0(1)$. By the identity obtained in Lemma 4, we can thus extend the definition of the Wigner function and view $W^\varepsilon(\psi)$ as a distribution acting on arbitrary subspaces of observables $\mathcal{O} \subset S_0^0(1)$ via

$$a \mapsto \langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^n)} \;=:\; \langle W^\varepsilon(\psi), a\rangle_{\mathcal{O}', \mathcal{O}} \,.$$

Besides boundedness, another important issue to be addressed is the sufficient condition for the positivity of a Weyl operator provided by the sharp Gårding inequality. It turns out, that non-negativity of the symbol $0 \leq a \in S_0^0(1)$, that is

$$\forall\, u \in \mathbb{C}^m\; \forall\, (q,p) \in \mathbb{R}^{2n} :\; \langle u, a(q,p)\, u\rangle_{\mathbb{C}^m} \;\geq\; 0\,,$$

is almost enough to guarantee non-negativity of the operator.

Theorem 6 (Semi-Classical Sharp Gårding Inequality) *Let* $0 \leq a \leq S_0^0(1)$ *be a non-negative symbol. Then, there is a positive constant* $C = C(a) > 0$ *such that for all* $\varepsilon > 0$ *and all* $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$

$$\langle \psi, a(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^n)} \;\geq\; -\,C\,\varepsilon\, \|\psi\|^2_{L^2(\mathbb{R}^n)} \,.$$

In the non-semi-classical context, Gårding proved a weaker result for strictly positive scalar symbols $a \geq \delta > 0$, while Hörmander [Ho] gave a proof for non-negative $a \geq 0$. In the matrix-valued case, the sharp Gårding inequality has first been proven by Lax and Nirenberg in [LaNi]. As indicated in Appendix A of [Je], the proof relying upon anti-Wick quantization also applies to matrix-valued operators. We refer to Part C, Proposition 5 later on for an application of this argument to symbols carrying an additional second scale.

7 Wigner Measures

Before, we have seen that for all $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$ the Wigner function $W^\varepsilon(\psi)$ is a distribution satisfying for all $a \in \mathcal{O} \subset S^0_0(1)$ a bound of the form

$$| \langle W^\varepsilon(\psi), a\rangle_{\mathcal{O}',\mathcal{O}} | \leq \; c_{2n}(a) \, \|\psi\|^2_{L^2(\mathbb{R}^n)} \,.$$

Hence, for a bounded sequence $(\psi^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^n, \mathbb{C}^m)$ we have

$$| \langle W^\varepsilon(\psi^\varepsilon), a\rangle_{\mathcal{O}',\mathcal{O}} | \leq \; c_{2n}(a) \, \sup_{\varepsilon>0} \|\psi^\varepsilon\|^2_{L^2(\mathbb{R}^n)} \,.$$

Since $S^0_0(1)$ is a separable topological vector space, an application of the Banach-Alaoglu Theorem, see Theorem 3.17 in [Ru], gives existence of a subsequence $(W^{\varepsilon_k}(\psi^{\varepsilon_k}))_{\varepsilon_k>0}$, which converges with respect to the weak*-topology in $S^0_0(1)'$. We denote such weak*-limit points by μ. By the sharp Gårding inequality we have for all non-negative $0 \leq a \in S^0_0(1)$

$$\begin{aligned}
\langle \mu, a\rangle_{\mathcal{O}',\mathcal{O}} \; &= \; \lim_{\varepsilon_k\to 0} \langle W^{\varepsilon_k}(\psi^{\varepsilon_k}), a\rangle_{\mathcal{O}',\mathcal{O}} \; = \; \lim_{\varepsilon_k\to 0} \langle \psi^{\varepsilon_k}, a(-i\varepsilon_k\nabla_q)\psi^{\varepsilon_k}\rangle_{L^2(\mathbb{R}^n)} \\
&\geq \; -\text{const.} \lim_{\varepsilon_k\to 0} \varepsilon_k \, \|\psi^{\varepsilon_k}\|^2_{L^2(\mathbb{R}^n)} \; = \; 0 \,,
\end{aligned}$$

implying that all the weak*-limit points μ are positive distributions. From this positivity one infers for all $a \in S^0_0(1)$

$$| \langle \mu, a\rangle_{\mathcal{O}',\mathcal{O}} | \leq \; \langle \mu, 1\rangle_{\mathcal{O}',\mathcal{O}} \, \|a\|_\infty \,,$$

for the detailed argument see the construction of two-scale Wigner measures later on. Hence, the distributions μ extend to bounded positive linear forms on the space of continuous, compactly supported functions $C_c(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$. By the Riesz representation theorem, the μ are positive bounded matrix-valued Radon measures on phase space $\mathbb{R}^{2n}$. That is, μ can uniquely be identified with a mapping

$$\mu : \; \mathcal{B}(\mathbb{R}^{2n}) \to \mathcal{L}_{pos}(\mathbb{C}^m)$$

from the Borel σ-algebra on $\mathbb{R}^{2n}$ to the positive hermitian $m \times m$-matrices, such that $\mu(\emptyset) = 0$ and $\mu(\bigcup_{j\in\mathbb{N}} B_j) = \sum_{j\in\mathbb{N}} \mu(B_j)$ for pairwise disjoint Borel sets $B_j \subset \mathbb{R}^{2n}$. For being a Radon measure μ has to satisfy $(\mathrm{tr}\mu)(B) = \sup\{(\mathrm{tr}\mu)(K) \mid K \subset B \text{ compact}\}$ for all Borel sets $B \subset \mathbb{R}^{2n}$.

Definition 3 (Wigner Measure) Let $(\psi^\varepsilon)_{\varepsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^n, \mathbb{C}^m)$. Then, the weak*-limit points μ in $S^0_0(1)'$ of the sequence of Wigner functions $(W^\varepsilon(\psi^\varepsilon))_{\varepsilon>0}$ are called *Wigner measures* or *semi-classical measures*.

The measures μ have been introduced under the name semi-classical measures by P. Gérard in [Ge2] and independently by P. L. Lions and T. Paul in [LiPa], who called them Wigner measures. [Ge2] refers for a proof of positivity to the construction of microlocal defect measures in [Ge1], which are the analogue of the measures μ in the context of pseudodifferential operators independent from a small parameter ε. There, positivity comes from smooth square roots of strictly positive symbols and subsequent application of the composition rule for pseudors. In [LiPa] positivity is obtained by Husimi functions, which are Wigner functions convoluted with Gaussians. This approach is similar in spirit to the use of anti-Wick symbols for the proof of the sharp Gårding inequality.

REMARK 5 We restate the key property of Wigner measures in this emphasizing remark. Wigner measures encode the limit of expectation values with respect to Weyl quantized operators. That is, for all smooth compactly supported functions $a \in C_c^\infty(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ we have

$$\int_{\mathbb{R}^{2n}} \mathrm{tr}(a(q,p)\mu(dq,dp)) \;=\; \lim_{\varepsilon_k \to 0} \langle \psi^{\varepsilon_k}, a(-i\varepsilon_k \nabla_q)\psi^{\varepsilon_k}\rangle_{L^2(\mathbb{R}^n)} \,.$$

$\diamondsuit$

As for examples, we return to the scalar semi-classical Gaussians $(g^\varepsilon)_{\varepsilon>0}$ defined in (2) and have a look at WKB type functions

$$\omega^\varepsilon(q) \;=\; a(q)\, e^{i f(q)/\varepsilon} \tag{23}$$

with amplitude $a \in C_c(\mathbb{R}^n, \mathbb{C})$ and phase $f \in C^1(\mathbb{R}^n, \mathbb{R})$. Both sequences have a unique Wigner measure. For the Gaussians g^ε, we infer from their Wigner functions (20) that their Wigner measure is the Dirac measure with mass in the point $(q_0, p_0) \in \mathbb{R}^{2n}$,

$$\mu(g^\varepsilon)(q,p) \;=\; \delta_{(p_0,q_0)}(q,p)\,.$$

For the WKB type functions ω^ε we calculate

$$\begin{aligned}
&\int_{\mathbb{R}^{2n}} W^\varepsilon(\omega^\varepsilon)(q,p)\, b(q,p)\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} e^{i y\cdot p}\, a(q - \tfrac{\varepsilon}{2} y)\, \overline{a}(q + \tfrac{\varepsilon}{2} y)\, e^{i(f(q-\frac{\varepsilon}{2}y) - f(q+\frac{\varepsilon}{2}y))/\varepsilon}\, b(q,p)\, dy\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} e^{i y\cdot(p - f^\varepsilon(y,q))}\, a(q - \tfrac{\varepsilon}{2} y)\, \overline{a}(q + \tfrac{\varepsilon}{2} y)\, b(q,p)\, dy\, dq\, dp\,,
\end{aligned}$$

where $f^\varepsilon(y,p) = \int_0^1 (1-t)\left(\nabla f(q - \frac{\varepsilon t}{2} y) + \nabla f(q + \frac{\varepsilon t}{2} y)\right) dt$ comes from a Taylor expansion. Since $f^\varepsilon(y,p) \to \nabla f(q)$ as $\varepsilon \to 0$, we have by dominated convergence

$$\begin{aligned}
&\lim_{\varepsilon\to 0} \int_{\mathbb{R}^{2n}} W^\varepsilon(\omega^\varepsilon)(q,p)\, b(q,p)\, dq\, dp \;= \\
&\quad (2\pi)^{-n} \int_{\mathbb{R}^{3n}} e^{i y\cdot(p - \nabla f(q))}\, |a(q)|^2\, b(q,p)\, dy\, dq\, dp \;=\; \int_{\mathbb{R}^{2n}} |a(q)|^2\, b(q, \nabla f(q))\, dq\, dp\,,
\end{aligned}$$

which means

$$\mu(\omega^\varepsilon)(q,p) \;=\; |a(q)|^2\, dq\; \delta_{\nabla f(q)}(p)\,.$$

For the Wigner function $W^\varepsilon(\psi)$ of arbitrary $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$ we have observed in (21), that its marginals are position density and semi-classically scaled momentum density. Identity (22) shows the consequent statement for the total mass. In general, the same does not hold for the Wigner measures μ, since in the limit $\varepsilon \to 0$ mass might move to infinity either in position or in momentum space. A simple pathological example is provided by a gliding bump, a sequence $(b^\varepsilon)_{\varepsilon>0}$ of the form

$$b^\varepsilon \;=\; b(\,\cdot\, - \varepsilon^{-1}) \quad \text{with} \quad 0 \neq b \in C_c(\mathbb{R}, \mathbb{C})\,.$$

Let $a \in C_c^\infty(\mathbb{R}, \mathbb{C})$ and $(\chi_j)_{j\in\mathbb{N}}$ a sequence in $C_c^\infty(\mathbb{R}, \mathbb{C})$ approximating the constant function $\mathbb{R} \to \mathbb{C}$, $p \mapsto 1$. Then, by dominated convergence, Remark 5, and Lemma 4,

$$\begin{aligned}
\int_{\mathbb{R}^{2n}} \operatorname{tr}(a(q)\,\mu(dq, dp)) \;&=\; \lim_{j\to\infty} \int_{\mathbb{R}^{2n}} \operatorname{tr}(a(q)\,\chi_j(p)\,\mu(dq, dp)) \\
&=\; \lim_{j\to\infty} \lim_{\varepsilon\to 0} \langle b^\varepsilon, (a\chi_j)(q, -i\varepsilon\nabla_q) b^\varepsilon\rangle_{L^2(\mathbb{R}^n)} \\
&=\; \lim_{j\to\infty} \lim_{\varepsilon\to 0} \int_{\mathbb{R}^{2n}} \operatorname{tr}(W^\varepsilon(b^\varepsilon)(q,p)\, a(q)\,\chi_j(p))\, dq\, dp\,.
\end{aligned}$$

By Lemma 3, we have $\pi_q(\operatorname{supp}(W^\varepsilon(b^\varepsilon))) \subset \overline{\operatorname{hull}(\operatorname{supp}(b^\varepsilon))}$. Since $\operatorname{supp}(b^\varepsilon) \cap \operatorname{supp}(a) = \emptyset$ for $\varepsilon > 0$ sufficiently small, we have shown that the projection of the measure μ onto position space equals zero and thus $\mu = 0$. Hence, we have for the gliding bump

$$0 \;=\; \mu(\mathbb{R}^2) \;\neq\; \lim_{\varepsilon\to 0} \|b^\varepsilon\|^2_{L^2(\mathbb{R})} \;=\; \|b\|^2_{L^2(\mathbb{R})}\,.$$

Retaining the Wigner functions' marginals and mass for the measures, one has to work with sequences of wave functions, which are localized in phase space.

Definition 4 (Localized in Phase Space) A sequence $(\psi^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^n, \mathbb{C}^m)$ is called *localized in phase space*, if it is compact at infinity, that is

$$\lim_{R\to\infty} \limsup_{\varepsilon\to 0} \int_{\{|q|\geq R\}} |\psi^\varepsilon(q)|^2\, dq \;=\; 0\,,$$

and ε-oscillatory, that is

$$\lim_{R\to\infty} \limsup_{\varepsilon\to 0} \varepsilon^{-n} \int_{\{|p|\geq R\}} \left|\widehat{\psi^\varepsilon}\left(\tfrac{p}{\varepsilon}\right)\right|^2 dp \;=\; 0\,.$$

We note, that compactness at infinity is synonymous to $(|\psi^\varepsilon|^2)_{\varepsilon>0}$ being tight in the space of positive measures, while an ε-oscillatory sequence oscillates at most with frequency $1/\varepsilon$, which is guaranteed, for example, if $\|\nabla\psi^\varepsilon\|_{L^2(\mathbb{R}^n)} \leq \text{const.}\,\varepsilon^{-1}$. All concrete examples $(\psi^\varepsilon)_{\varepsilon>0}$ we meet in this dissertation, except the preceding gliding bump, are localized in phase space.

Proposition 2 *Let $(\psi^\varepsilon)_{\varepsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^n, \mathbb{C}^m)$, which is localized in phase space, and let μ be an associated Wigner measure. Then,*

$$\operatorname{tr}(\mu(\mathbb{R}^{2n})) \;=\; \lim_{\varepsilon_k\to 0} \|\psi^{\varepsilon_k}\|^2_{L^2(\mathbb{R}^n)}\,,$$

and we have for all $a \in C_b(\mathbb{R}^n, \mathcal{L}(\mathbb{C}^m))$

$$\begin{aligned}
\int_{\mathbb{R}^{2n}} a(q)\,\mu(dq,dp) &= \lim_{\varepsilon_k \to 0} \int_{\mathbb{R}^n} a(q)\,\psi^{\varepsilon_k}(q) \otimes \overline{\psi^{\varepsilon_k}(q)}\,dq\,,\\
\int_{\mathbb{R}^{2n}} a(p)\,\mu(dq,dp) &= \lim_{\varepsilon_k \to 0} (2\pi\varepsilon_k)^{-n} \int_{\mathbb{R}^n} a(p)\,\widehat{\psi^{\varepsilon_k}}\big(\tfrac{p}{\varepsilon_k}\big) \otimes \overline{\widehat{\psi^{\varepsilon_k}}\big(\tfrac{p}{\varepsilon_k}\big)}\,dp\,.
\end{aligned}$$

For a proof, we refer to Proposition 1.7 in [GMMP] or Proposition 4 in [TePa]. There, the above identities are shown by means of semi-classical Weyl calculus, a horse to be ridden to death later on.

REMARK 6 Taking traces in the last two equations of Proposition 2, one obtains for bounded sequences $(\psi^\varepsilon)_{\varepsilon>0}$, which are localized in phase space,

$$\begin{aligned}
\int_{\mathbb{R}^n} (\mathrm{tr}\mu)(\cdot,dp) &= \mathrm{w}-\lim_{\varepsilon_k \to 0} \int_{\mathbb{R}^n} |\psi^{\varepsilon_k}(q)|^2\,dq\,,\\
\int_{\mathbb{R}^n} (\mathrm{tr}\mu)(dq,\cdot) &= \mathrm{w}-\lim_{\varepsilon_k \to 0} (2\pi\varepsilon_k)^{-n} \int_{\mathbb{R}^n} \big|\widehat{\psi^{\varepsilon_k}}\big(\tfrac{p}{\varepsilon_k}\big)\big|^2\,dp\,,
\end{aligned}$$

where the weak limits are meant in the space of bounded positive measures. $\diamondsuit$

In general, a bounded sequence of wave functions might have several Wigner measures. The characterization of a unique Wigner measure is provided by the following observation.

PROPOSITION 3 (UNIQUENESS) *Let* $(\psi^\varepsilon)_{\varepsilon>0}$ *be a bounded sequence in* $L^2(\mathbb{R}^n, \mathbb{C}^m)$ *and* $\psi \in L^2(\mathbb{R}^n, \mathbb{C}^m)$.

1. *If* $\psi^\varepsilon \to \psi$ *strongly in* $L^2(\mathbb{R}^2, \mathbb{C}^m)$ *as* $\varepsilon \to 0$, *then* $(\psi^\varepsilon)_{\varepsilon>0}$ *admits a unique Wigner measure* μ *with*

$$\mu(q,p) \;=\; \big(\psi(q) \otimes \overline{\psi}(q)\big)\,dq\,\delta_0(p)\,, \qquad (q,p) \in \mathbb{R}^{2n}\,. \tag{24}$$

2. *If* $(\psi^\varepsilon)_{\varepsilon>0}$ *is localized in phase space and admits a Wigner measure* μ *of the form (24), then there is a subsequence* $(\psi^{\varepsilon_k})_{\varepsilon_k>0}$ *such that* $\psi^{\varepsilon_k} \to \psi$ *strongly in* $L^2(\mathbb{R}^n, \mathbb{C}^m)$ *as* $\varepsilon_k \to 0$.

The proof combines various arguments given in Section III of [LiPa].

PROOF. Let $\psi^\varepsilon \to \psi$ strongly as $\varepsilon \to 0$. Then,

$$\psi^\varepsilon(q - \tfrac{\varepsilon}{2}\,y) \otimes \overline{\psi^\varepsilon}(q + \tfrac{\varepsilon}{2}\,y) \;\rightharpoonup\; \psi(q) \otimes \overline{\psi}(q) \quad \text{in} \quad \mathcal{S}'(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))\,.$$

Indeed,

$$\begin{aligned}
\psi^\varepsilon(q - \tfrac{\varepsilon}{2}\,y) \otimes \overline{\psi^\varepsilon}(q + \tfrac{\varepsilon}{2}\,y) &= \psi^\varepsilon(q - \tfrac{\varepsilon}{2}\,y) \otimes \big(\overline{\psi^\varepsilon}(q + \tfrac{\varepsilon}{2}\,y) - \overline{\psi}(q + \tfrac{\varepsilon}{2}\,y)\big)\\
&+ \big(\psi^\varepsilon(q - \tfrac{\varepsilon}{2}\,y) - \psi(q - \tfrac{\varepsilon}{2}\,y)\big) \otimes \overline{\psi}(q + \tfrac{\varepsilon}{2}\,y)\\
&+ \psi(q - \tfrac{\varepsilon}{2}\,y) \otimes \overline{\psi}(q + \tfrac{\varepsilon}{2}\,y)\\
&=: I_1^\varepsilon(q,y) + I_2^\varepsilon(q,y) + I_3^\varepsilon(q,y)\,,
\end{aligned}$$

where for all $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$

$$\begin{aligned}\left|\int_{\mathbb{R}^{2n}} I_1^\varepsilon(q,y)\, a(q,y)\, dq\, dy\right| &\leq \int_{\mathbb{R}^n} \sup_{q\in\mathbb{R}^n} |a(q,y)|\, dy \sup_{y\in\mathbb{R}^n} \left|\int_{\mathbb{R}^n} I_1^\varepsilon(q,y)\, dq\right| \\ &\leq \int_{\mathbb{R}^n} \sup_{q\in\mathbb{R}^n} |a(q,y)|\, dy\ \|\psi^\varepsilon\|_{L^2(\mathbb{R}^n)}\, \|\psi^\varepsilon - \psi\|_{L^2(\mathbb{R}^n)} \to 0\,,\end{aligned}$$

and analogously

$$\left|\int_{\mathbb{R}^{2n}} I_2^\varepsilon(q,y)\, a(q,y)\, dq\, dy\right| \to 0\,,$$

while by dominated convergence

$$\int_{\mathbb{R}^{2n}} I_3^\varepsilon(q,y)\, a(q,y)\, dq\, dy \to \int_{\mathbb{R}^{2n}} \psi(q) \otimes \overline{\psi}(q)\, a(q,y)\, dq\, dy$$

as $\varepsilon \to 0$. Hence, by the Fourier inversion formula

$$\begin{aligned}&\int_{\mathbb{R}^{2n}} W^\varepsilon(\psi^\varepsilon)(q,p)\, a(q,p)\, dq\, dp \\ &= (2\pi)^{-n} \int_{\mathbb{R}^{3n}} e^{i\,y\cdot p}\, \psi^\varepsilon(q - \tfrac{\varepsilon}{2} y) \otimes \overline{\psi^\varepsilon}(q + \tfrac{\varepsilon}{2} y)\, a(q,p)\, dy\, dq\, dp \\ &\to (2\pi)^{-n} \int_{\mathbb{R}^{3n}} e^{i\,y\cdot p}\, \psi(q) \otimes \overline{\psi}(q)\, a(q,p)\, dy\, dq\, dp = \int_{\mathbb{R}^n} \psi(q) \otimes \overline{\psi}(q)\, a(q,0)\, dq\,,\end{aligned}$$

which gives (24).
For proving the converse statement, let $(\psi^\varepsilon)_{\varepsilon>0}$ be localized in phase space admitting a Wigner measure μ of the form (24). By Proposition 2, we then have

$$\lim_{\varepsilon_k\to 0} \|\psi^{\varepsilon_k}\|^2_{L^2(\mathbb{R}^n)} = \mathrm{tr}(\mu(\mathbb{R}^{2n})) = \int_{\mathbb{R}^n} |\psi(q)|^2\, dq = \|\psi\|^2_{L^2(\mathbb{R}^n)}\,.$$

Since $(\psi^\varepsilon)_{\varepsilon>0}$ is bounded in $L^2(\mathbb{R}^n, \mathbb{C}^m)$, we can assume without loss of generality that the previous subsequence $(\psi^{\varepsilon_k})_{\varepsilon_k>0}$ is weakly convergent in $L^2(\mathbb{R}^n, \mathbb{C}^m)$. However, convergence of norms together with weak convergence implies the claimed strong convergence. □

8 Weyl Calculus

Let $a_j \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$ for $j \in \{1,2\}$. One immediately verifies that

$$a_j(q, -i\varepsilon\nabla_q) : \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)\,, \qquad j \in \{1,2\}.$$

Hence, the composition $a_1(q, -i\varepsilon\nabla_q) \circ a_2(q, -i\varepsilon\nabla_q) =: B$ is a well-defined operator mapping Schwartz functions into Schwartz functions. A tedious calculation reveals that B is a Weyl quantized operator with symbol $b \in \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m))$, which can be written as

$$b(q,p) = (a_1 \sharp_\varepsilon a_2)(q,p) := \left(\exp\left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})\right) a_1(q,p) a_2(q',p')\right)|_{q=q',p=p'}\,,$$

where the exponentiation of the differential operator $\frac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})$ is meant in the sense of the functional calculus provided by the spectral theorem, and D_x is short-hand for $-i\nabla_x$, $x \in \mathbb{R}^n$. On suitable symbol classes, there is an asymptotic expansion of the ε-scaled Moyal product $\sharp_\varepsilon$, which turns the Weyl correspondence into a powerful calculus.

Definition 5 (Order Function) A positive function $m : \mathbb{R}^{2n} \to]0,\infty[$ is called an *order function*, if there exist positive constants $C > 0$ and $N > 0$ with

$$\forall x, y \in \mathbb{R}^{2n} : \ m(x) \le C \langle x - y\rangle^N m(y),$$

where $\langle x\rangle := \sqrt{1 + |x|^2}$ denotes the Japanese bracket.

The order functions to be used in the following are constant functions and powers of the Japanese bracket. Also the pointwise product of two order functions is an order function itself. Following Chapter 7 in [DiSj], we define the function space

$$S(m) := \left\{ a \in C^\infty(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m)) \mid \forall \alpha \in \mathbb{N}_0^{2n}\ \exists C_\alpha > 0\ \forall x \in \mathbb{R}^{2n} : \ |\partial^\alpha a(x)| \le C_\alpha\, m(x) \right\}.$$

Equipped with the topology, which is induced by the family of semi-norms

$$\|(\partial^\alpha a)(\cdot)\, m^{-1}(\cdot)\|_\infty, \qquad \alpha \in \mathbb{N}_0^{2n},$$

the space $S(m)$ is a Fréchet space. For $k \in \mathbb{R}$ and $\delta \in [0, 1/2]$ one defines the symbol class

$$\begin{aligned} S^k_\delta(m) := \Big\{ & a : \mathbb{R}^{2n}\times]0,1] \to \mathcal{L}(\mathbb{C}^m) \ \Big|\ \forall \varepsilon \in]0,1] : \ a(\cdot\,;\varepsilon) \in S(m), \\ & \forall \alpha \in \mathbb{N}_0^{2n}\ \exists C_\alpha > 0\ \forall (x,\varepsilon) \in \mathbb{R}^{2n}\times]0,1] : \ |\partial^\alpha a(x;\varepsilon)| \le C_\alpha\, m(x)\, \varepsilon^{-\delta|\alpha| - k} \Big\}. \end{aligned}$$

Formulating the Calderón-Vaillancourt Theorem, we have already met the symbol class $S^0_0(1)$ of smooth functions, which are bounded together with all their derivatives. The parameter δ encodes the loss in ε after differentiation. Besides the friendly $\delta = 0$, we will also encounter the more unpleasant $\delta = 1/2$.

Remark 7 Let $k \in \mathbb{R}$, $\delta \in [0, 1/2]$, and m an order function. For $a \in S^k_\delta(m)$, the Weyl quantized operator $a(q, -i\varepsilon\nabla_q)$ is a continuous linear map $\mathcal{S}(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}(\mathbb{R}^n, \mathbb{C}^m)$ from Schwartz functions to Schwartz functions, and a continuous linear map $\mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m) \to \mathcal{S}'(\mathbb{R}^n, \mathbb{C}^m)$ from temperate distributions to temperate distributions. The Calderón-Vaillancourt Theorem also extends to symbols in $S^0_\delta(1)$ with $\delta \in [0, 1/2]$. That is, for $a \in S^0_\delta(1)$ we have $a(q, -i\varepsilon\nabla_q) \in \mathcal{L}(L^2(\mathbb{R}^n, \mathbb{C}^m))$ and

$$\|a(q, -i\varepsilon\nabla_q)\|_{\mathcal{L}(L^2(\mathbb{R}^n))} \le c_{2n}(a).$$

For a proof of these remarks see Lemma 7.8 and Theorem 7.11 in [DiSj]. $\diamondsuit$

Definition 6 (Asymptotic Expansion) Let $\delta \in [0, 1/2]$ and m an order function. For $a \in S^{k_0}_\delta(m)$ and a sequence $(a_j)_{j\in\mathbb{N}}$ with $a_j \in S^{k_j}_\delta(m)$ and $k_j \searrow -\infty$ as $j \nearrow \infty$ we define

$$a \sim \sum_{j=0}^\infty a_j \quad \text{in} \quad S^{k_0}_\delta(m),$$

if $\left(a-\sum_{j=0}^{N} a_j\right) \in S_\delta^{k_{N+1}}(m)$ for all $N \in \mathbb{N}_0$.
The symbols a_0 and a_1 are called the *principal* and the *subprincipal symbol* of a.

With these notions of symbol classes and asymptotic expansions within them, one obtains well-definedness and in most cases an asymptotic expansion of the Moyal product.

LEMMA 5 *Let m_1 and m_2 be order functions.*

1. *For $\delta \in [0,1/2]$, the bilinear map*

$$\sharp_\varepsilon : \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m)) \times \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m)) \to \mathcal{S}(\mathbb{R}^{2n}, \mathcal{L}(\mathbb{C}^m)) \tag{25}$$

extends continuously to a map $S_\delta^0(m_1) \times S_\delta^0(m_2) \to S_\delta^0(m_1 m_2)$. If $\delta < 1/2$, then

$$(a_1 \sharp_\varepsilon a_2)(q,p) \sim \sum_{j=0}^{\infty} \tfrac{1}{j!} \left(\left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'}) \right)^j a_1(q,p) a_2(q',p') \right) \Big|_{q=q',p=p'} \tag{26}$$

in $S_\delta^0(m_1 m_2)$ for all $a_j \in S_0^0(m_j)$ with $j \in \{1,2\}$.

2. *For $(\delta_1, \delta_2) \in \{(0,1/2),(1/2,0)\}$, the Moyal product (25) extends continuously to a map*

$$S_{\delta_1}^0(m_1) \times S_{\delta_2}^0(m_2) \to S_{1/2}^0(m_1 m_2)\,,$$

and the asymptotic expansion (26) holds in $S_{1/2}^0(m_1 m_2)$ for all $a_j \in S_{\delta_j}^0(m_j)$ with $j \in \{1,2\}$.

PROOF. The first claim is proven in Proposition 7.7 in [DiSj]. Hence, we just have to deal with the second assertion. It is enough to prove the case $(\delta_1,\delta_2) = (0,1/2)$. By Proposition 7.6 in [DiSj], the map

$$\exp\!\left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})\right) : \mathcal{S}(\mathbb{R}^{4n}, \mathcal{L}(\mathbb{C}^m)) \to \mathcal{S}(\mathbb{R}^{4n}, \mathcal{L}(\mathbb{C}^m))$$

extends continuously to an operator $S_{1/2}^0(m_1 \otimes m_2) \to S_{1/2}^0(m_1 \otimes m_2)$. Thus, we only have to show the asymptotic expansion. Observing, that every differentiation of a_2 produces a factor $\varepsilon^{-1/2}$, it is clear that

$$b_j := \tfrac{1}{j!} \left(\left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'}) \right)^j a_1(q,p) a_2(q',p') \right) \Big|_{q=q',p=p'} \in S_{1/2}^{-j/2}(m_1 m_2)\,.$$

Proving that $\left(a_1 \sharp_\varepsilon a_2 - \sum_{j=0}^{N} b_j\right) \in S_{1/2}^{-(N+1)/2}(m_1 m_2)$, one defines the smooth mapping

$$E : \quad \mathbb{R} \to \mathcal{L}(S_{1/2}^0(m_1 \otimes m_2))\,, \quad t \mapsto E(t) := \exp\left(\tfrac{it}{2}(D_p D_{q'} - D_q D_{p'})\right)\,.$$

Taylor expansion of order N around $t = 0$ gives

$$E(\varepsilon) = \sum_{j=0}^{N} \varepsilon^j \tfrac{1}{j!} (\partial_t^j E)(0) + \varepsilon^{N+1} \tfrac{1}{N!} \int_0^1 (1-t)^N (\partial_t^{N+1} E)(\varepsilon t)\, dt\,.$$

The first summand is nothing else than

$$\sum_{j=0}^{N} \tfrac{1}{j!} \left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})\right)^j ,$$

while the remainder term can be rewritten as

$$\tfrac{1}{N!} \int_0^1 (1-t)^N \left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})\right)^{N+1} E(\varepsilon t)\, dt .$$

Since $E(\varepsilon t)$ preserves the symbol class $S^0_{1/2}(m_1 \otimes m_2)$, and since every differentiation of $a_1(q,p)a_2(q',p')$ produces an extra factor $\varepsilon^{-1/2}$,

$$\int_0^1 (1-t)^N \left(\tfrac{i\varepsilon}{2}(D_p D_{q'} - D_q D_{p'})\right)^{N+1} E(\varepsilon t)\, a_1(q,p)\, a_2(q',p')\, dt\, |_{q'=q,p'=p}$$

is a symbol in $S^{-(N+1)/2}_{1/2}(m_1 m_2)$, and we are done. □

Remark 8 Let $\delta \in [0, 1/2]$, m_1, m_2 be order functions, and $a_j \in S^0_\delta(m_j)$ with $j \in \{1,2\}$. Then,

$$a_1(q, -i\varepsilon\nabla_q) \circ a_2(q, -i\varepsilon\nabla_q) \;=\; (a_1 \sharp_\varepsilon a_2)(q, -i\varepsilon\nabla_q)$$

either as mappings on Schwartz functions or as mappings on temperate distributions. A proof of this claim relies on Lemma 5 and a density argument, see Theorem 7.9 in [DiSj]. ♢

We will not use the asymptotic expansion of Lemma 5 in its full glory, but just with its very first terms. In the sequel, we will meet with annoying repetition identities like

$$a_1(q, -i\varepsilon\nabla_q) \circ a_2(q, -i\varepsilon\nabla_q) \;=\; (a_1 a_2)(q, -i\varepsilon\nabla_q) + \mathcal{O}(\varepsilon)$$

for $a_j \in S^0_0(1)$ with $j \in \{1,2\}$, where the big-oh is meant in the space of bounded operators on $L^2(\mathbb{R}^n, \mathbb{C}^m)$. If we have one of the symbols in $S^0_0(1)$ and the other one in $S^0_{1/2}(1)$, then we obtain

$$a_1(q, -i\varepsilon\nabla_q) \circ a_2(q, -i\varepsilon\nabla_q) \;=\; (a_1 a_2)(q, -i\varepsilon\nabla_q) + \mathcal{O}(\sqrt{\varepsilon}) .$$

For *scalar-valued* symbols $a_j \in S^0_0(1)$, one approximates the commutator by

$$[a_1(q, -i\varepsilon\nabla_q), a_2(q, -i\varepsilon\nabla_q)] \;=\; -i\varepsilon\, \{a_1, a_2\}(q, -i\varepsilon\nabla_q) + \mathcal{O}(\varepsilon^3) , \tag{27}$$

where

$$\{a_1, a_2\}(q,p) \;=\; \partial_p a_1(q,p)\, \partial_q a_2(q,p) - \partial_q a_1(q,p)\, \partial_p a_2(q,p) , \qquad (q,p) \in \mathbb{R}^{2n}$$

denotes the Poisson bracket of the two smooth functions a_1 and a_2. We note, that equation (27) relies on the vanishing of the commutator $[a_1, a_2]$ as well as the skew-symmetry of the Poisson bracket $\{a_1, a_2\} = -\{a_2, a_1\}$ for scalar-valued symbols a_j. The vanishing of the term involving ε^2 and second order derivatives of a_1 and a_2 is due to the special symmetry of Weyl quantization and again the scalar-valuedness of the a_j. If one of the symbols involved is polynomial, then the asymptotic expansion of the Moyal product terminates. Especially for scalar-valued polynomials a_j of degree less or equal than two and semi-classical parameter $\varepsilon = 1$ we have

$$[a_1(q, -i\nabla_q), a_2(q, -i\nabla_q)] \;=\; -i\{a_1, a_2\}(q, -i\nabla_q)\,,$$

which shows a correspondence of the Lie algebra structure on the side of the Weyl quantized operators and of the symbols. By the Theorem of Groenewold, see for example Theorem 4.59 in [Fo], scalar-valued polynomials of degree two are indeed the largest class of symbols, for which any quantization procedure can acchieve a correspondence between commutator and Poisson bracket. Not only with this respect Weyl quantization is optimal. For general matrix-valued symbols $a_j \in S^0_0(1)$, we have to accept the less pleasant

$$[a_1(q, -i\varepsilon\nabla_q), a_2(q, -i\varepsilon\nabla_q)] \;=\; [a_1, a_2]\,(q, -i\varepsilon\nabla_q) + \mathcal{O}(\varepsilon)\,,$$

or if the symbols commute, $[a_1, a_2] = 0$,

$$[a_1(q, -i\varepsilon\nabla_q), a_2(q, -i\varepsilon\nabla_q)] \;=\; -\tfrac{i\varepsilon}{2}\left(\{a_1, a_2\} - \{a_2, a_1\}\right)(q, -i\varepsilon\nabla_q) + \mathcal{O}(\varepsilon^2)\,.$$

We emphasize at this point, that for matrix-valued functions, the Poisson bracket is no more skew-symmetric, a fact forbidding the extension of some convenient arguments well-established in the analyis of scalar Weyl operators to the case of systems. A simple example for non-skew-symmetry is given by

$$\{a, a\} \;=\; \begin{pmatrix} 0 & -2 \\ 2 & 0 \end{pmatrix} \neq 0 \qquad \text{for} \qquad a(q,p) \;=\; \begin{pmatrix} q & p \\ p & -q \end{pmatrix},\ (q,p) \in \mathbb{R}^2\,.$$

As an application for the just developed calculus we prove that the solution of our favourite model problem (1) inherits the property of being localized in phase space from the initial data.

Proposition 4 (Localized in Phase Space) *Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ be the solution of the Schrödinger system (1) for a bounded sequence of initial data $(\psi^\varepsilon_0)_{\varepsilon>0}$ in $L^2(\mathbb{R}^2, \mathbb{C}^2)$, which is localized in phase space. Then, also $(\psi^\varepsilon(t))_{\varepsilon>0}$ is localized in phase space for all $t \in \mathbb{R}$.*

Proof. We choose some smooth functions $\chi \in C^\infty(\mathbb{R}^2, \mathbb{R})$ and $\widetilde{\chi} \in C^\infty_c(\mathbb{R}^4, \mathbb{R})$ with

$$\chi(p) = 0 \quad \text{for} \quad |p| < 1/2\,, \qquad \chi(p) = 1 \quad \text{for} \quad |p| > 1\,,$$

and

$$\widetilde{\chi}(q,p) = 1 \quad \text{for} \quad |(q,p)| < 1/2\,, \qquad \widetilde{\chi}(q,p) = 0 \quad \text{for} \quad |(q,p)| > 1\,.$$

We set $\chi_R(p) = \chi(p/R)$ and $\widetilde{\chi}_N(q,p) = \widetilde{\chi}(q/N, p/N)$ for $N, R > 0$. By the Calderón-Vaillancourt Theorem, the Weyl quantized operators $\chi_R(-i\varepsilon\nabla_q)$ and $\widetilde{\chi}_N(q, -i\varepsilon\nabla_q)$ are both bounded operators on $L^2(\mathbb{R}^2, \mathbb{C}^2)$, and we have $\widetilde{\chi}_N(q, -i\varepsilon\nabla_q) \to 1$ in $\mathcal{L}(L^2(\mathbb{R}^2, \mathbb{C}^2))$ as $N \to \infty$. The composed operator

$$C^\varepsilon_{N,R} \;:=\; \widetilde{\chi}_N(q, -i\varepsilon\nabla_q) \circ \chi_R(-i\varepsilon\nabla_q) \;=\; (\widetilde{\chi}_N \,\sharp_\varepsilon\, \chi_R)(q, -i\varepsilon\nabla_q)$$

has a symbol $\widetilde{\chi}_N \sharp_\varepsilon \chi_R \in \mathcal{S}(\mathbb{R}^4, \mathbb{C})$, which is a Schwartz function on phase space. Hence, $C^\varepsilon_{N,R}$ is regularizing, see Remark 4. We want to show that $(\psi^\varepsilon(t))_{\varepsilon>0}$ is ε-oscillatory, which will be acchieved by proving

$$\lim_{R\to\infty} \limsup_{\varepsilon\to 0} \int_{\mathbb{R}^2} |\, \chi_R(-i\varepsilon\nabla_q)\, \psi^\varepsilon(t,q)\,|^2 \; dq \;=\; 0\,.$$

Since

$$\lim_{N\to\infty} \int_{\mathbb{R}^2} |\, C^\varepsilon_{N,R}\, \psi^\varepsilon(t,q)\,|^2 \; dq \;=\; \int_{\mathbb{R}^2} |\, \chi_R(-i\varepsilon\nabla_q)\, \psi^\varepsilon(t,q)\,|^2 \; dq\,,$$

we study $w^\varepsilon_{N,R}(t) := C_{N,R}\, \psi^\varepsilon(t)$. If $\psi^\varepsilon(t)$ is the solution of (1) for an initial datum $\psi^\varepsilon_0 \in D(H^\varepsilon)$, then $w^\varepsilon_{N,R}(t) \in D(H^\varepsilon)$ for all $t \in \mathbb{R}$, the mapping $t \mapsto w^\varepsilon_{N,R}(t)$ is continuously differentiable, and we have

$$i\varepsilon\, \partial_t w^\varepsilon_{N,R}(t) \;=\; C^\varepsilon_{N,R}\, H^\varepsilon\, \psi^\varepsilon(t)\,.$$

Moreover, $C^\varepsilon_{N,R}\, H^\varepsilon = H^\varepsilon\, C^\varepsilon_{N,R} - [H^\varepsilon, C^\varepsilon_{N,R}]$ on $D(H^\varepsilon)$. Denoting the symbols of H^ε and $C^\varepsilon_{N,R}$ by $h(q,p) = \frac{1}{2}|p|^2 + V(q)$ and $c^\varepsilon_{N,R}(q,p)$, respectively, we have

$$h \sharp_\varepsilon c^\varepsilon_{N,R} - c^\varepsilon_{N,R} \sharp_\varepsilon h \;=\; \tfrac{\varepsilon}{2i}\left(\{V, c^\varepsilon_{N,R}\} - \{c^\varepsilon_{N,R}, V\}\right)\,.$$

Hence, by the linearity of V, the commutator $M^\varepsilon_{N,R} := [H^\varepsilon, C^\varepsilon_{N,R}]$ is a bounded operator on $L^2(\mathbb{R}^2, \mathbb{C}^2)$, whose norm $\|M^\varepsilon_{N,R}\|_{\mathcal{L}} \le \text{const.}\ \varepsilon/R$ can be bounded independently from $N \in \mathbb{N}$. We rewrite the evolution of $w^\varepsilon_{N,R}(t,q)$ as

$$i\varepsilon\, \partial_t w^\varepsilon_{N,R}(t) \;=\; H^\varepsilon\, w^\varepsilon_{N,R}(t) + M^\varepsilon_{N,R}\, \psi^\varepsilon(t)$$

and obtain by the symmetry of H^ε

$$\tfrac{d}{dt}\, \|w^\varepsilon_{N,R}(t)\|^2_{L^2(\mathbb{R}^2)} \;\le\; \text{const.}\ \varepsilon^{-1}\, \|M^\varepsilon_{N,R}\|_{\mathcal{L}(L^2(\mathbb{R}^2))}\, \|\psi^\varepsilon(t)\|_{L^2(\mathbb{R}^2)}\, \|w^\varepsilon_{N,R}(t)\|_{L^2(\mathbb{R}^2)}\,.$$

Since $(\psi^\varepsilon(t))_{\varepsilon>0}$ is bounded in $L^2(\mathbb{R}^2, \mathbb{C}^2)$ uniformly for all times $t \in \mathbb{R}$, we obtain

$$\|w^\varepsilon_R(t)\|_{L^2(\mathbb{R}^2)} \;\le\; \|w^\varepsilon_R(0)\|_{L^2(\mathbb{R}^2)} \;+\; \text{const.}\, t/R\,.$$

Passing to the limits $N \to \infty$, $\varepsilon \to 0$, and $R \to \infty$, we get that $(\psi^\varepsilon(t))_{\varepsilon>0}$ is ε-oscillatory for all times $t \in \mathbb{R}$. For general initial data $\psi^\varepsilon_0 \in L^2(\mathbb{R}^2, \mathbb{C}^2)$, one chooses an approximating sequence $(\phi^\varepsilon_n)_{n\in\mathbb{N}}$ in $D(H^\varepsilon)$ with $\sup_{\varepsilon>0} \|\phi^\varepsilon_n - \psi^\varepsilon_0\|_{L^2} \to 0$ $n \to \infty$. Then,

$$\lim_{R\to\infty} \limsup_{\varepsilon\to 0} \|\chi_R(-i\varepsilon\nabla_q)\, e^{-i H^\varepsilon t/\varepsilon}\, \psi^\varepsilon_0\|_{L^2(\mathbb{R}^2)} \;\le\; \sup_{R>0} c_4(\chi_R)\, \sup_{\varepsilon>0} \|\phi^\varepsilon_n - \psi^\varepsilon_0\|_{L^2(\mathbb{R}^n)} \;\to\; 0$$

as $n \to \infty$. Proving that $(\psi^\varepsilon(t))_{\varepsilon>0}$ is compact at infinity, one replaces $\chi_R(-i\varepsilon\nabla_q)$ by $\chi_R(q)$ and proceeds analogously. □

9 Classical Transport

Discussing the local version of Born-Oppenheimer approximation in Section 2.3 of Part A, we have mentioned that Egorov's Theorem provides approximate control on the unitary time evolution. With all the basics of Weyl calculus at hand, we can now formulate this important theorem and also sketch its proof.

9.1 Egorov's Theorem

Theorem 7 (Egorov) *Let* m *be an order function and* $\lambda \sim \sum_{j=0}^{\infty} \lambda_j \in S_0^0(m)$ *a scalar-valued symbol with*

$$\partial_q^\alpha \partial_p^\beta \lambda_j \in L^\infty(\mathbb{R}^{2n}, \mathbb{C}), \qquad \alpha, \beta \in \mathbb{N}_0^n,\ j \in \mathbb{N}_0,\ |\alpha| + |\beta| + j \geq 2,$$

whose Weyl operator $\Lambda^\varepsilon = \lambda(q, -i\varepsilon\nabla_q)$ *is an essentially self-adjoint operator acting in* $L^2(\mathbb{R}^n, \mathbb{C})$. *Then, for all scalar-valued* $a \in S_0^0(1)$ *and* $t \in \mathbb{R}$ *there exists a scalar-valued* $a(t) \in S_0^0(m)$ *such that*

$$e^{i\Lambda^\varepsilon t/\varepsilon}\, a(q, -i\varepsilon\nabla_q)\, e^{-i\Lambda^\varepsilon t/\varepsilon} \;=\; a(t)(q, -i\varepsilon\nabla_q) \tag{28}$$

and $a(t) \sim \sum_{j=0}^{\infty} a_j(t)$ *in* $S_0^0(m)$ *uniformly on compact time intervals with*

$$a_0(t) \;=\; a \circ \Phi^t,$$

where $\Phi^t : \mathbb{R}^{2n} \to \mathbb{R}^{2n}$ *is the flow of the Hamiltonian system*

$$\dot q \;=\; \nabla_p \lambda_0(q,p), \qquad \dot p \;=\; -\nabla_q \lambda_0(q,p).$$

associated with the principal symbol λ_0 *of* λ.

We refer for a complete proof to Theorem IV.10 in [Ro] and just sketch the basic idea.

Sketch of Proof. On some dense set the left hand side of (28) is continuously differentiable with respect to t. Denoting it by $A(t)$, we obtain the Heisenberg equation

$$-i\varepsilon \tfrac{d}{dt} A(t) \;=\; [\Lambda^\varepsilon, A(t)], \qquad A(0) = a(q, -i\varepsilon\nabla_q).$$

Assuming that $A(t) = a(t)(q, -i\varepsilon\nabla_q)$ for some symbol $a(t)$, the Heisenberg equation means on the symbol level

$$-i\varepsilon \tfrac{d}{dt} a(t) \;=\; \lambda \sharp_\varepsilon a(t) - a(t) \sharp_\varepsilon \lambda, \qquad a(0) = a.$$

Inserting an asymptotic expansion $\sum_{j=0}^{\infty} a_j(t)$ of $a(t)$ and expanding the Moyal product asymptotically according to Lemma 5, we get for the zeroth order term in ε

$$\tfrac{d}{dt} a_0(t) \;=\; \{\lambda_0, a_0(t)\}, \qquad a_0(0) = a,$$

or equivalently $a_0(t) = a \circ \Phi^t$, where global existence of the flow Φ^t comes from the essential self-adjointness of $\lambda(q, -i\varepsilon\nabla_q)$. In this way one determines order by order equations for the $a_j(t)$ and finally proves, that the such constructed symbol $a(t)$ does the job. □

9.2 Transport of Wigner Functions and Measures

Egorov's Theorem has as an immediate corollary an approximate description for the dynamics of the Wigner function $W^\varepsilon(\psi^\varepsilon(t))$ of the solution $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^n, \mathbb{C}))$ of

$$i\varepsilon\partial_t \psi^\varepsilon \;=\; \Lambda^\varepsilon \psi^\varepsilon, \qquad \psi^\varepsilon(0) = \psi_0^\varepsilon, \tag{29}$$

where $(\psi_0^\varepsilon)_{\varepsilon>0}$ is a bounded sequence of initial data in $L^2(\mathbb{R}^n, \mathbb{C})$. For the Hamilton operator Λ^ε we assume the same properties as in Theorem 7.

COROLLARY 2 *Let* $\psi^\varepsilon(t)$ *be the solution of (29) and* $W^\varepsilon(\psi^\varepsilon(t))$ *its Wigner function. Then, we have for all* $t \in \mathbb{R}$ *and* $a \in \mathcal{S}(\mathbb{R}^{2n}, \mathbb{C})$

$$\int_{\mathbb{R}^{2n}} \big(W^\varepsilon(\psi^\varepsilon(t)) - W^\varepsilon(\psi_0^\varepsilon) \circ \Phi^{-t}\big)(q,p)\, a(q,p)\, dq\, dp \;=\; \mathcal{O}(\varepsilon)$$

as $\varepsilon \to 0$. *On compact time intervals the above approximation holds uniformly in* t.

PROOF. We have for all scalar-valued $a \in S_0^0(1)$ and $t \in \mathbb{R}$

$$\begin{aligned}
\langle W^\varepsilon(\psi^\varepsilon(t)), a\rangle_{\mathcal{O}',\mathcal{O}} &= \big\langle e^{-i\Lambda^\varepsilon t/\varepsilon}\psi_0^\varepsilon\,, a(q,-i\varepsilon\nabla_q)\, e^{-i\Lambda^\varepsilon t/\varepsilon}\psi_0^\varepsilon\big\rangle_{L^2(\mathbb{R}^n)} \\
&= \big\langle \psi_0^\varepsilon\,, (a\circ\Phi^t)(q,-i\varepsilon\nabla_q)\,\psi_0^\varepsilon\big\rangle_{L^2(\mathbb{R}^n)} \;+\; \varepsilon\,\langle\psi_0^\varepsilon\,, R^\varepsilon\,\psi_0^\varepsilon\rangle_{L^2(\mathbb{R}^n)}
\end{aligned}$$

with $R^\varepsilon \in \mathcal{L}(L^2(\mathbb{R}^n,\mathbb{C}))$ such that $\sup_{\varepsilon>0}\|R^\varepsilon\|_{\mathcal{L}(L^2)} < \infty$. Hence,

$$\langle W^\varepsilon(\psi^\varepsilon(t)), a\rangle_{\mathcal{O}',\mathcal{O}} \;=\; \big\langle W^\varepsilon(\psi_0^\varepsilon), a\circ\Phi^t\big\rangle_{\mathcal{O}',\mathcal{O}} \;+\; \mathcal{O}(\varepsilon)\,.$$

By Lemma 4 we obtain the claimed

$$\int_{\mathbb{R}^{2n}} W^\varepsilon(\psi^\varepsilon(t))(q,p)\, a(q,p)\, dq\, dp \;=\; \int_{\mathbb{R}^{2n}} (W^\varepsilon(\psi_0^\varepsilon)\circ\Phi^{-t})(q,p)\, a(q,p)\, dq\, dp \;+\; \mathcal{O}(\varepsilon)\,.$$

□

The unitary time evolution preserves the L^2-norm, that is $\|\psi^\varepsilon(t)\|_{L^2(\mathbb{R}^n)} = \|\psi_0^\varepsilon\|_{L^2(\mathbb{R}^n)}$ for all $t \in \mathbb{R}$. Hence, the sequence $(\psi^\varepsilon(t))_{\varepsilon>0}$ admits Wigner measures $\mu(t)$ for every $t \in \mathbb{R}$. However, for different points of time t there might be different subsequences $(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t)))_{\varepsilon_k>0}$ weakly converging to the limit points $\mu(t)$, even the number of different limit points might differ for different points of time. Thus, a priori the continuity of the Wigner function

$$W^\varepsilon(\psi^\varepsilon(t)) \in C(\mathbb{R}, L^2(\mathbb{R}^{2n},\mathbb{C}))$$

does not seem to translate into a continuous time dependance of the Wigner measures $\mu(t)$. However:

COROLLARY 3 *Let* $(\psi^\varepsilon(t))_{\varepsilon>0}$ *be the sequence of solutions of (29). If the sequence of initial Wigner functions* $(W^{\varepsilon_k}(\psi_0^{\varepsilon_k}))_{\varepsilon_k>0}$ *converges weakly to a Wigner measure* μ_0, *then* $(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t)))_{\varepsilon_k>0}$ *converges weakly to a Wigner measure* $\mu(t)$ *for all* $t \in \mathbb{R}$. *On compact time intervals the convergence is uniform. Moreover, for all* $t \in \mathbb{R}$

$$\mu(t) \;=\; \mu_0 \circ \Phi^{-t}\,,$$

and $\mu(t) \in C(\mathbb{R}, \mathcal{M}_b^+(\mathbb{R}^{2n}))$, *where* $\mathcal{M}_b^+(\mathbb{R}^{2n}) = C_c(\mathbb{R}^{2n},\mathbb{C})'$ *denotes the space of positive bounded Radon measures on* $\mathbb{R}^{2n}$ *equipped with the weak dual topology.*

PROOF. By Egorov's Theorem, we have for all $t \in \mathbb{R}$ and $a \in S_0^0(1)$

$$\langle W^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\rangle_{\mathcal{O}',\mathcal{O}} \;=\; \langle W^{\varepsilon_k}(\psi_0^{\varepsilon_k}), a(t)\rangle_{\mathcal{O}',\mathcal{O}}\,.$$

Hence, the left and the right hand side of the preceding equation converge as $\varepsilon_k \to 0$, and we have

$$\langle \mu(t), a \rangle_{\mathcal{O}', \mathcal{O}} \;=\; \langle \mu_0, a(t) \rangle_{\mathcal{O}', \mathcal{O}} \,.$$

The proof of the uniform convergence on compact time intervals requires an application of the Arzela-Ascoli Theorem, for which we refer to the proof of Proposition 7 later on. Corollary 2 immediately implies $\mu(t) = \mu_0 \circ \Phi^{-t}$. Hence, it remains to show the asserted continuity of $t \mapsto \mu(t)$. We have for $a \in C_c(\mathbb{R}^{2n}, \mathbb{C})$ and $t, s \in \mathbb{R}$

$$\begin{aligned} \Big| \int_{\mathbb{R}^{2n}} a(q,p)\,(\mu(t) - \mu(s))(dq,dp) \Big| \;&=\; \Big| \int_{\mathbb{R}^{2n}} (a \circ \Phi^t - a \circ \Phi^s)(q,p)\,\mu_0(dq,dp) \Big| \\ &\le\; \mu_0(\mathbb{R}^{2n})\, \| a \circ \Phi^t - a \circ \Phi^s \|_\infty \;\longrightarrow\; 0 \end{aligned}$$

as $s \to t$, since a is uniformly continuous. □

The single-band operators $\Lambda^\varepsilon_\pm = \frac{\varepsilon^2}{2}\,\Delta_q^{A^\pm} + E^\pm(q)$ of our central model problem are essentially self-adjoint operators with domain $C_c^\infty(\mathbb{R}^2, \mathbb{C})$. They have as their principal symbol the continuous functions $\lambda_0^\pm(q,p) = \frac{1}{2}|p|^2 + E^\pm(q) = \frac{1}{2}|p|^2 \pm |q|$, which are smooth away from the crossing manifold $\{q = 0\}$. This lack of smoothness hinders a direct application of Egorov's Theorem as formulated above. One has to employ a smooth cut-off around the crossing manifold to circumvent this problem, see the proof of Proposition 7 in Part C later on. Nevertheless, we may ask how the scalar-valued Wigner functions of the solutions $\psi^\varepsilon_\pm(t)$ of the two one-band equations (13) with initial data

$$\psi^\varepsilon_\pm(0,q) \;=\; \psi^\varepsilon_{0,\pm}(q) \;:=\; \langle \psi^\varepsilon_0(q), \chi^\pm(q) \rangle_{\mathbb{C}^2}$$

relate to the matrix-valued Wigner function of the solution $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ of the full model system (1) with initial datum $\psi^\varepsilon_0 \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. The following Lemma helps clarifying this question. It proves, that Wigner transformation and projection onto the eigenspaces commute up to an error of order ε.

Lemma 6 *Let $(\psi^\varepsilon)_{\varepsilon > 0}$ be a bounded sequence in $L^2(\mathbb{R}^2, \mathbb{C}^2)$. We decompose*

$$\psi^\varepsilon(q) \;=\; \psi^\varepsilon_+(q)\,\chi^+(q) \;+\; \psi^\varepsilon_-(q)\,\chi^-(q)\,,$$

where $\chi^\pm \in C^\infty(\mathbb{R}^2, \mathbb{C}^2)$ are the smooth eigenvectors defined in (12). Then, there exists a subsequence $(\varepsilon_k)_{k \in \mathbb{N}}$ with $\varepsilon_k \to 0$ as $k \to \infty$, such that for all scalar observables $a \in C_c^\infty(\mathbb{R}^4, \mathbb{C})$ with $\mathrm{supp}(a) \cap \{q = 0\} = \emptyset$

$$\begin{aligned} &\lim_{\varepsilon_k \to 0} \int_{\mathbb{R}^4} W^{\varepsilon_k}(\psi^{\varepsilon_k}_\pm)(q,p)\; a(q,p)\, dq\, dp \;= \\ &\qquad \lim_{\varepsilon_k \to 0} \int_{\mathbb{R}^4} \mathrm{tr}\,\big(W^{\varepsilon_k}(\psi^{\varepsilon_k})(q,p)\; \Pi^\pm(q)\; a(q,p)\; \Pi^\pm(q) \big)\, dq\, dp\,, \end{aligned}$$

where $\Pi^\pm(q) = \chi^\pm(q)\,\overline{\chi^\pm(q)}^{\,t} \in C^\infty(\mathbb{R}^2 \setminus \{0\}, \mathcal{L}_{\mathrm{sa}}(\mathbb{C}^2))$ are the eigen projectors of the linear conical crossing potential $V(q)$.

Proof. The existence of the sequence $(\varepsilon_k)_{k\in\mathbb{N}}$, such that both limits exist, is obtained by an application of the Banach-Alaoglu Theorem, Theorem 3.17 in [Ru]. Hence, we just have to show coincidence of the two limits. We have for $\varepsilon > 0$

$$\int_{\mathbb{R}^4} W^\varepsilon(\psi^\varepsilon_\pm)(q,p)\; a(q,p)\; dq\,dp \;=\; \left\langle \psi^\varepsilon_\pm, a(q,-i\varepsilon\nabla_q)\,\psi^\varepsilon_\pm\right\rangle_{L^2(\mathbb{R}^2)}$$
$$= \left\langle \overline{\chi^\pm}\cdot\psi^\varepsilon, a(q,-i\varepsilon\nabla_q)\,\overline{\chi^\pm}\cdot\psi^\varepsilon\right\rangle_{L^2(\mathbb{R}^2)} \;=\; \left\langle \psi^\varepsilon, \chi^\pm\, a(q,-i\varepsilon\nabla_q)\,\overline{\chi^\pm}^{\,t}\;\psi^\varepsilon\right\rangle_{L^2(\mathbb{R}^2)}.$$

Now, by Weyl calculus

$$\chi^\pm(q)\,a(q,-i\varepsilon\nabla_q)\,\overline{\chi^\pm(q)}^{\,t} \;=\; \big(\chi^\pm\, a\,\overline{\chi^\pm}^{\,t}\big)(q,-i\varepsilon\nabla_q) + \mathcal{O}(\varepsilon)\,,$$

where the $\mathcal{O}(\varepsilon)$ is meant in the space of bounded operators on $L^2(\mathbb{R}^2,\mathbb{C}^2)$. Moreover, since $a(q,p)\in\mathbb{C}$ is scalar and has support away from the crossing, we have

$$\chi^\pm\, a\,\overline{\chi^\pm}^{\,t} \;=\; a\,\Pi^\pm \;=\; \Pi^\pm\, a\,\Pi^\pm \in C^\infty_c(\mathbb{R}^4,\mathbb{C})\,.$$

Hence,

$$\begin{aligned}
\lim_{\varepsilon_k\to 0}\int_{\mathbb{R}^4} & W^{\varepsilon_k}(\psi^{\varepsilon_k}_\pm)(q,p)\; a(q,p)\; dq\,dp \\
&= \lim_{\varepsilon_k\to 0}\left\langle \psi^{\varepsilon_k}, \chi^\pm\, a(q,-i\varepsilon_k\nabla_q)\,\overline{\chi^\pm}^{\,t}\;\psi^{\varepsilon_k}\right\rangle_{L^2(\mathbb{R}^2)} \\
&= \lim_{\varepsilon_k\to 0}\left\langle \psi^{\varepsilon_k}, (\Pi^\pm\, a\,\Pi^\pm)(q,-i\varepsilon_k\nabla_q)\,\psi^{\varepsilon_k}\right\rangle_{L^2(\mathbb{R}^2)} \\
&= \lim_{\varepsilon_k\to 0}\int_{\mathbb{R}^4} \mathrm{tr}\,\big(W^{\varepsilon_k}(\psi^{\varepsilon_k})(q,p)\;\Pi^\pm(q)\; a(q,p)\;\Pi^\pm(q)\big)\,dq\,dp\,.
\end{aligned}$$

□

Let $(\psi^\varepsilon_0)_{\varepsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^2,\mathbb{C}^2)$ and $[0,T]$ a compact time interval, in which the solution $\psi^\varepsilon(t) = e^{-iH^\varepsilon t/\varepsilon}\,\psi^\varepsilon_0$ of the model system (1) has phase space support outside the crossing up to order ε. For such an time interval $[0,T]$, there exists an open set $U\subset\mathbb{R}^4$ with $\{q=0\}\subset U$ such that

$$\int_{\mathbb{R}^4} W^\varepsilon(\psi^\varepsilon(t))(q,p)\,a(q,p)\,dq\,dp \;=\; \mathcal{O}(\varepsilon) \tag{30}$$

for all $a\in C^\infty_c(\mathbb{R}^4,\mathcal{L}(\mathbb{C}^2))$ with $\mathrm{supp}(a)\subset U$.

Adiabatic Decoupling. The local Born-Oppenheimer theory discussed in Section 2.3 together with Lemma 6 yields for all $t\in[0,T]$

$$\begin{aligned}
\lim_{\varepsilon_k\to 0}\int_{\mathbb{R}^4} & W^{\varepsilon_k}(\psi^{\varepsilon_k}_\pm(t))(q,p)\; a(q,p)\; dq\,dp \;= \\
& \lim_{\varepsilon_k\to 0}\int_{\mathbb{R}^4} \mathrm{tr}\,\big(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t))(q,p)\;\Pi^\pm(q)\; a(q,p)\;\Pi^\pm(q)\big)\,dq\,dp
\end{aligned}$$

for all $a\in C^\infty_c(\mathbb{R}^4,\mathbb{C})$ with $\mathrm{supp}(a)\cap\{q=0\}=\emptyset$. Proposition 7 later on shows, that for all times $t\in[0,T]$ the same sequence $(\varepsilon_k)_{k\in\mathbb{N}}$ can be chosen, and that the above limits are even uniform on $[0,T]$. In the language of Wigner measures we have proven the following. If $\mu^\pm(t)$ denotes a Wigner measure of $\psi^\varepsilon_\pm(t) \in L^2(\mathbb{R}^2,\mathbb{C})$ and $\mu(t)$ a Wigner measure of $\psi^\varepsilon(t) \in L^2(\mathbb{R}^2,\mathbb{C}^2)$, then for all $t \in [0,T]$

$$\mu^\pm(t)(B) \;=\; \mathrm{tr}(\mu(t)\,\Pi^\pm)(B)$$

for all Borel sets $B \subset \mathbb{R}^4$ with $B \cap \{q=0\} = \emptyset$.

Born-Oppenheimer approximation. Since the projectors $\Pi^\pm(q)$ are rank one projectors, we can write the diagonal components of the Wigner function $W^\varepsilon(\psi^\varepsilon(t))$ as

$$\Pi^\pm\, W^\varepsilon(\psi^\varepsilon(t))\,\Pi^\pm \;=\; \mathrm{tr}(W^\varepsilon(\psi^\varepsilon(t))\,\Pi^\pm)\,\Pi^\pm \;=:\; w^\varepsilon_\pm(t)\,\Pi^\pm\,.$$

We obtain by the preceding discussion, that for time intervals $[0,T]$, in which $\psi^\varepsilon(t)$ has phase space support outside the crossing $\{q=0\}$ up to order ε,

$$\int_{\mathbb{R}^4} \big(w^\varepsilon_\pm(t) - w^\varepsilon_\pm(0)\circ\Phi^{-t}_\pm\big)(q,p)\,a(q,p)\,dq\,dp \;=\; \mathcal{O}(\varepsilon) \tag{31}$$

for all $a \in C^\infty_c(\mathbb{R}^4,\mathbb{C})$ with $\mathrm{supp}(a)\cap\{q=0\} = \emptyset$. The flows $\Phi^t_\pm : \mathbb{R}^4 \to \mathbb{R}^4$ belong to the Hamiltonian systems

$$\dot q(t) \;=\; p(t)\,, \qquad \dot p(t) \;=\; \mp\tfrac{q(t)}{|q(t)|}\,, \tag{32}$$

which stem from the Hamilton functions $\lambda^\pm_0 = \frac{1}{2}|p|^2 \pm |q|$. We have to be aware of the discontinuity of $\nabla_q\,\lambda^\pm_0 = \pm q/|q|$ at $q=0$ and postpone a more sorrow discussion of the flows $\Phi^t_\pm$ to the following Section 9.3. We also mention, that Proposition 7 later on provides an alternative, more contiguous proof of (31). Regardless of its various proofs, the given approximation motivates the definition of a Born-Oppenheimer function

$$W^\varepsilon_{\mathrm{BO}}(t) \;:=\; \big(w^\varepsilon_+(0)\circ\Phi^{-t}_+\big)\,\Pi^+ + \big(w^\varepsilon_-(0)\circ\Phi^{-t}_-\big)\,\Pi^- \;\in L^2(\mathbb{R}^4,\mathcal{L}(\mathbb{C}^2))$$

for $t \in \mathbb{R}$. In this notation, identity (31) is rephrased as follows. For all times $t\in[0,T]$, for which the phase space support condition (30) is satisfied within the time interval $[0,T]$, one has

$$\int_{\mathbb{R}^4} \mathrm{tr}\Big(\big(W^\varepsilon(\psi^\varepsilon(t)) - W^\varepsilon_{\mathrm{BO}}(t)\big)(q,p)\;a(q,p)\Big)\,dq\,dp \;=\; \mathcal{O}(\varepsilon) \tag{33}$$

for all diagonal observables $a \in C^\infty_c(\mathbb{R}^4,\mathcal{L}(\mathbb{C}^2))$ with

$$\big[a(q,p),V(q)\big] \;=\; \Big[a(q,p),\begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}\Big] \;=\; 0$$

and $\mathrm{supp}(a)\cap\{q=0\}=\emptyset$. A final, more sloppy variant of formulating the leading order time-dependent Born-Oppenheimer approximation defines the groups

$$\mathcal{L}^t_\pm : \quad L^2(\mathbb{R}^4,\mathbb{C}) \to L^2(\mathbb{R}^4,\mathbb{C})\,, \quad w \mapsto w\circ\Phi^{-t}_\pm$$

and rewrites the approximate dynamics of the diagonal components $w^\varepsilon_\pm(t)$ as

$$\begin{pmatrix} w^\varepsilon_+(t) \\ w^\varepsilon_-(t) \end{pmatrix} \;\approx\; \underbrace{\begin{pmatrix} \mathcal{L}^t_+ & 0 \\ 0 & \mathcal{L}^t_- \end{pmatrix}}_{=:\,\mathcal{L}^t_0}\begin{pmatrix} w^\varepsilon_+(0) \\ w^\varepsilon_-(0) \end{pmatrix}. \tag{34}$$

Away from the crossing manifold, the group $\mathcal{L}_0^t$ gives an approximation to the real dynamics associated with the Schrödinger system (1) up to an error of order ε. There, we observe adiabatic decoupling and semi-classical behaviour of the wave function. To overcome the crossing, we will replace the *group* $\mathcal{L}_0^t$ by an asymptotic *semigroup* $\mathcal{L}_\varepsilon^t$, which takes the adiabatic transfer at the crossing manifold into account. The construction of such a semigroup $\mathcal{L}_\varepsilon^t$ will be the aim of Section 10 in Part C.

9.3 The Model System

The Hamiltonian systems (32) are equivalent to the Newtonian equations

$$\ddot{q} \;=\; -\nabla_q E^{\pm}(q)\,, \tag{35}$$

with central field $E^{\pm}(q) = \pm|q|$. Trajectories, which never hit the crossing $\{q = 0\}$, are well-defined, even smoothly depending on time. Hence, our first question is to ask for the set of initial data, which issue the critical trajectories touching the crossing manifold. The easy answer is given by the conservation of angular momentum for Newtonian motion in a central field,

$$\exists\, t \in \mathbb{R}: \; \Phi_{\pm}^t(q_0, p_0) \cap \{q = 0\} \neq \emptyset \qquad \Longleftrightarrow \qquad M_0 := q_0 \wedge p_0 = 0$$

with $q \wedge p := q^{\perp} \cdot p = q_1 p_2 - q_2 p_1$. The second conserved quantity is the total energy

$$E_0^{\pm} \;:=\; \lambda_0^{\pm}(q_0, p_0) \;=\; \tfrac{1}{2}|p_0|^2 \pm |q_0|\,.$$

We start by discussing the dynamics for initial data with zero angular momentum.

Lemma 7 (Zero Angular Momentum) *Choosing initial data* $(q_0, p_0) \in \mathbb{R}^4 \setminus \{0\}$ *with* $q_0 \wedge p_0 = 0$, *we study the solutions of the two Hamiltonian systems (32). Then, the trajectory associated with the Hamilton function* $\lambda_0^+(q,p) = \frac{1}{2}|p|^2 + |q|$ *is the first to hit* $\{q = 0\}$ *for a positive time* $t_0 > 0$,

$$t_0 \;=\; p_0 \cdot \omega + \sqrt{|p_0|^2 + 2|q_0|}\,,$$

where $\omega = \frac{q_0}{|q_0|}$ *for* $q_0 \neq 0$ *and* $\omega = \frac{p_0}{|p_0|}$ *for* $q_0 = 0$. *Moreover, we have for* $t \in [0, t_0[$

$$q^{\pm}(t) \;=\; \mp \tfrac{1}{2}\, t^2\, \omega + t\, p_0 + q_0, \qquad p^{\pm}(t) \;=\; \mp\, t\omega + p_0\,.$$

Proof. First, we insert a Taylor expansion of $q^{\pm}(t)$ into (32) and obtain $\frac{q^{\pm}(t)}{|q^{\pm}(t)|} \to \omega$ as $t \to 0^+$. Since the zero angular momentum is conserved for all times, we rewrite $q^{\pm}(t) = k^{\pm}(t)\omega$ and $p^{\pm}(t) = l^{\pm}(t)\omega$ with $k^{\pm}(t), l^{\pm}(t) \in \mathbb{R}$, and are left with the differential equations

$$\dot{k} \;=\; l\,, \qquad \dot{l} \;=\; \mp 1\,, \qquad k(0) = k_0\,, \qquad l(0) = l_0\,.$$

Since $q^{\pm}(t) = t\, p_0 + o(t)$, we have $k_0 = |q_0|$. Moreover, $l_0 = \mathrm{sgn}(q_0 \cdot p_0)|p_0|$ if $q_0 \neq 0$ and $l_0 = |p_0|$ if $q_0 = 0$. Thus, we have $l^{\pm}(t) = \mp t + l_0$ and $k^{\pm}(t) = \mp\frac{1}{2}\, t^2 + l_0 t + k_0$. The determinant for the zeros of $k^{\pm}(t)$ is $l_0^2 \pm 2k_0$. We distinct different cases.

If $l_0^2 < 2k_0$, then only $q^+(\cdot)$ hits $\{q = 0\}$ for some positive time $t_0 > 0$, i. e. for $t_0 = l_0 + (l_0^2 + 2k_0)^{1/2}$.

If $l_0^2 = 2k_0$, then $q^+(\cdot)$ hits $\{q = 0\}$ for some $t_0 > 0$, before $q^-(\cdot)$ does so. The hitting time is given by $t_0 = l_0 + |l_0|\sqrt{2}$.

If $l_0^2 > 2k_0$, then we have to distinguish two cases. If $\mathrm{sgn}(l_0) > 0$, then only $q^+(\cdot)$ has a positive hitting time t_0, and we get again $t_0 = l_0 + (l_0^2 + 2k_0)^{1/2}$. If $\mathrm{sgn}(l_0) < 0$, then the $q^-(\cdot)$ also has a positive hitting time $s_0 = |l_0| - (l_0^2 - 2k_0)^{1/2}$. However, an easy calculation gives $t_0 < s_0$, and we are done.

$\square$

The preceding proof contains the following observation concerning trajectories of (32) with Hamiltonian function $\lambda_0^-(q, p) = \frac{1}{2}|p|^2 - |q|$.

Remark 9 The trajectory of (32) with Hamilton function $\lambda_0^-(q, p) = \frac{1}{2}|p|^2 - |q|$ and initial datum $q^-(0) = 0$, $p^-(0) = p_0 \neq 0$ is given for positive times $t > 0$ by

$$q^-(t) \;=\; \left(\frac{t^2}{2|p_0|} + t\right) p_0\,, \qquad p^-(t) \;=\; \left(\frac{t}{|p_0|} + 1\right) p_0\,.$$

This trajectory does not hit $\{q = 0\}$ for times $t > 0$ and goes off to infinity, $|q^-(t)| \to \infty$ as $t \to \infty$. $\diamondsuit$

By the proof of Lemma 7, we can also explicitly derive the recurrent hitting times of the trajectories associated with $\lambda_0^+(q, p) = \frac{1}{2}|p|^2 + |q|$.

Remark 10 The trajectory of (32) with Hamilton function $\lambda_0^+(q, p) = \frac{1}{2}|p|^2 + |q|$ and initial datum $q^+(0) = q_0 \neq 0$, $p^+(0) = p_0$ with $q_0 \wedge p_0 = 0$ hits the crossing manifold $\{q = 0\}$ recurrently for positive times $t_j > 0$,

$$t_j \;=\; p_0 \cdot \omega + (2j + 1)L\,, \qquad j \in \mathbb{N}_0\,,$$

with $\omega = \frac{q_0}{|q_0|}$ and $L = \sqrt{|p_0|^2 + 2|q_0|}$. For times $t \in \,]t_j, t_{j+1}[$, $j \in \mathbb{N}_0$, we have

$$q^+(t) \;=\; (-1)^j \big(\tfrac{1}{2}(t - t_j)^2 - L(t - t_j)\big)\omega\,, \qquad p^+(t) \;=\; (-1)^j\,(t - t_j - L)\,\omega\,.$$

This explicit formulae show $p^+(t_j) = (-1)^{j+1}\,L\omega \neq 0$ for all $j \in \mathbb{N}_0$, a change of direction for $q^+(\cdot)$ at the crossing $\{q = 0\}$, and boundedness of the motion, that is $|q^+(t)| \leq L^2/2$ for all $t > 0$. $\diamondsuit$

Summarizing, we have seen that trajectories $(q^\pm(\cdot), p^\pm(\cdot))$ passing through the crossing at some positive time $t_* > 0$ are well-defined and have a unique continuous continuation through the crossing, as long as $p^\pm(t_*) \neq 0$. Hence, the only point in phase space prohibiting a straightforward definition of the Hamiltonian flows $\Phi^t_\pm$ is the origin $(0, 0) \in \mathbb{R}^4$. Denoting the zero-energy shells by $(\lambda_0^\pm)^{-1}(0) := \{(q, p) \in \mathbb{R}^4 \mid \lambda_0^\pm(q, p) = 0\}$, we have $(\lambda_0^+)^{-1}(0) = \{(0, 0)\}$ and define for $t \in \mathbb{R}$

$$\begin{aligned}
\Phi^t_+(q_0,p_0) &= (q^+(t),p^+(t)) \quad \text{for} \quad (q_0,p_0) \notin (\lambda_0^+)^{-1}(0)\,,\\
\Phi^t_+(q_0,p_0) &= (q_0,p_0) \qquad\qquad\quad \text{for} \quad (q_0,p_0) \in (\lambda_0^+)^{-1}(0)\,.
\end{aligned}$$

The mapping $\mathbb{R}^4 \to \mathbb{R}^4$, $(q,p) \mapsto \Phi^t_+(q,p)$ is continuous for all $t \in \mathbb{R}$. For the minus-flow Φ^t_-, the definition is less elegant. Denoting the hypersurface of zero angular momentum by

$$I \;=\; \left\{(q,p) \in \mathbb{R}^4 \mid q \wedge p = 0\right\},$$

we set for $t \in \mathbb{R}$

$$\begin{aligned}
\Phi^t_-(q_0,p_0) &= (q^-(t),p^-(t)) \quad \text{for} \quad (q_0,p_0) \notin (\lambda_0^-)^{-1}(0) \cap I\,,\\
\Phi^t_-(q_0,p_0) &= (q_0,p_0) \qquad\qquad\quad \text{for} \quad (q_0,p_0) \in (\lambda_0^-)^{-1}(0) \cap I\,.
\end{aligned}$$

The thus defined mapping $(q,p) \mapsto \Phi^t_-(q,p)$ is continuous only outside the codimension two set $(\lambda_0^-)^{-1}(0) \cap I = \left\{(q,p) \in \mathbb{R}^4 \mid q = \pm\frac{|p|}{2}\,p\right\}$. However, both flows $\{\Phi^t_\pm(q,p)\}_{t\in\mathbb{R}}$ form a group for all $(q,p) \in \mathbb{R}^4$. Before turning to a more thorough study of the dynamics with non-zero angular momentum, we whish to draw the reader's attention to Figure 6, which anticipatingly discusses the implications of the zero angular momentum case for the approximate dynamics of the Schrödinger system (1). Propagating initial data (q_0,p_0) with non-zero $M_0 = q_0 \wedge p_0 \neq 0$, we switch to polar coordinates $q = r(\cos\varphi, \sin\varphi)$ with $(r,\varphi) \in [0,\infty[\times[0,2\pi[$ and rewrite the Newtonian equation (35) as

$$\dot r^2 \;=\; 2\left(E_0^\pm - V^\pm(r)\right), \qquad \dot\varphi \;=\; M_0\, r^{-2}\,, \tag{36}$$

where

$$V^\pm(r) \;:=\; \pm r + \tfrac12\, M_0^2\, r^{-2}$$

is the effective potential energy, see Chapter 2.8 in [Ar]. We have for the solutions $r^\pm(t)$ of the radial part of (36)

$$\forall\, t \in \mathbb{R}: \quad V^\pm(r^\pm(t)) \;\le\; E_0^\pm\,.$$

Therefore, we look for the $r \geq 0$ with

$$P^\pm(r) \;:=\; \mp 2\, r^3 + 2\, E_0^\pm\, r^2 - M_0^2 \;\geq\; 0\,.$$

The discriminants $D^\pm$ of the cubic polynomials $P^\pm$ are given by

$$D^\pm \;=\; -\tfrac{1}{729}\,(E_0^\pm)^6 \;+\; \tfrac14\left(\mp\tfrac{2}{27}(E_0^\pm)^3 \;\pm\; \tfrac12\, M_0^2\right)^2 \;=\; \tfrac12\, M_0^2\left(\tfrac18\, M_0^2 \;-\; \tfrac{1}{27}\,(E_0^\pm)^3\right).$$

First, we concentrate on the dynamics associated with the upper electronic level and discuss the polynomial $P^+(r) = -2\,r^3 + 2\,E_0^+\,r^2 - M_0^2$, which is monotonously increasing for $r \in\,]0, 2\,E_0^+/3[$ and monotonously decreasing outside this interval. If we write $p_0 = k\,q_0/|q_0| + l\,q_0^\perp/|q_0|$ with $k,l \in \mathbb{R}$, then $l = M_0/|q_0|$ and $E_0^+ = \frac12\,k^2 + \frac12\,(M_0/|q_0|)^2 + |q_0|$. The function $s \mapsto e(s) = \frac12\,k^2 + \frac12(M_0/s)^2 + s$ attains its minimum for $s = M_0^{2/3}$. Thus, $E_0^+ \geq e(M_0^{2/3}) \geq \frac32\,M_0^{2/3}$, and we always have $D^+ \leq 0$.

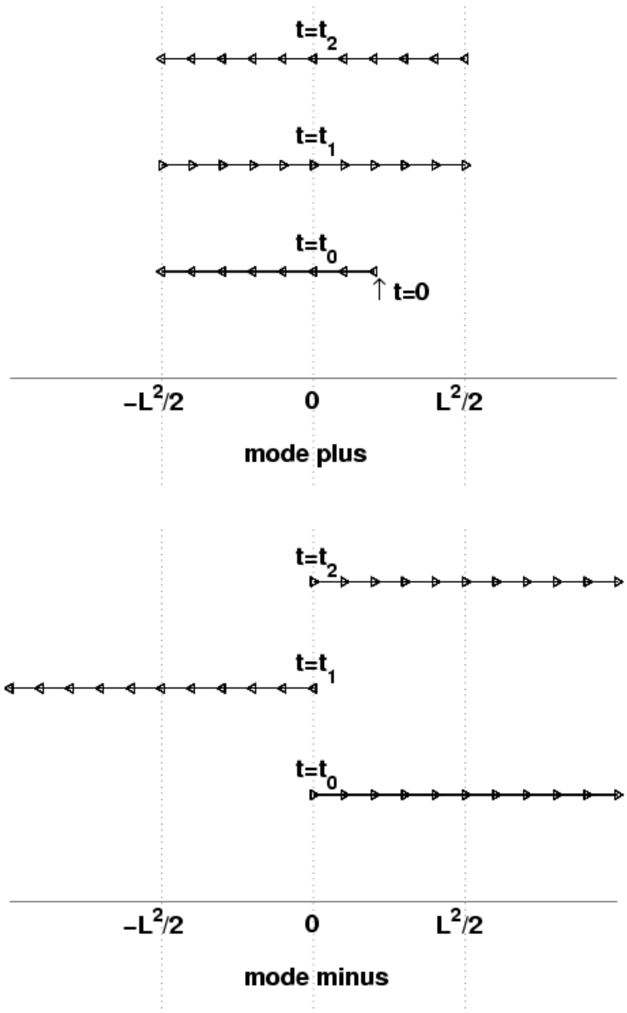


Figure 6: We anticipate what the preceding discussion of the classical dynamics means for a zeroth order approximation in ε of the Wigner functions $w^\varepsilon_\pm(t)$ introduced in Section 9.2. We assume $w^\varepsilon_-(0) = 0$ and consider a point $(q_0, p_0) \in \text{supp}(w^\varepsilon_+(0))$ with $q_0 \wedge p_0 = 0$ and $q_0 \neq 0$. The q-component of the trajectory $(q^+(\cdot), p^+(\cdot))$ for this initial datum runs along the straight line given by $\omega = q_0/|q_0|$. It hits $\{q = 0\}$ at time $t = t_0$ for the first time, propagating a part of w^ε_+ into the crossing and initiating a non-adiabatic transition onto the lower electronic level. A trajectory $(q^-(\cdot), p^-(\cdot))$ starts off into the opposite direction, with which the trajectory $(q^+(\cdot), p^+(\cdot))$ has entered the crossing, and carries some part of w^ε_- off to infinity. The trajectory $(q^+(\cdot), p^+(\cdot))$ hits $\{q = 0\}$ again at time $t = t_1$, and initiates another non-adiabatic transfer onto the lower level, and so on. Thus, we have bounded oscillations for w^ε_+ and recurrent creation of parts of w^ε_-, which eventually go off to infinity. We become more precise in Part C, where we also provide the Landau-Zener formula encoding the correct rate of non-adiabatic transfer and encorporate the trajectories, which just come close by the crossing.

Lemma 8 (Upper Electronic Level) *The Newtonian equation of motion*

$$\ddot{q}(t) \;=\; -\tfrac{q(t)}{|q(t)|}\,, \qquad q(0) \;=\; q_0\,, \qquad \dot{q}(0) \;=\; p_0$$

with initial datum $(q_0, p_0) \in \mathbb{R}^4$ *of non-zero angular momentum* $M_0 = q_0 \wedge p_0 \neq 0$ *has two different types of solution.*

1. Circular motion: *If* $27\,M_0^2 = 8\,(E_0^+)^3$ *with* $E_0^+ = \frac{1}{2}|p_0|^2 + |q_0|$, *then the orbit is a circle with radius* $R_0 = 2\,E_0^+/3$, *which is revolved with constant angular velocity* $\sqrt{1/R_0}$.

2. Oscillations in an annulus: *If* $27\,M_0^2 < 8\,(E_0^+)^3$, *then there exist* $R_1, R_3 > 0$ *with* $R_3 < 2\,E_0^+/3 < R_1 < E_0^+$ *such that the solution stays inside the non-degenerate annulus* $\{q \in \mathbb{R}^2 \mid R_3 \leq |q| \leq R_1\}$. *The radial motion is periodic, while the angular motion varies monotonously.*

Proof. We start with the case $D^+ = 0$, that is $27\,M_0^2 = 8\,(E_0^+)^3$. Then, the polynomial $P^+(r)$ has a repeated real root $b \in \mathbb{R}$. Factorizing $P^+(r) = -2\,(r-a)(r-b)^2$, we get $2ab^2 = -M_0^2$ and $a + 2b = E_0^+ > 0$. Therefore, $a < 0 < b$, and by the monotonicity properties of $P^+(r)$, $b = 2\,E_0^+/3$. Thus, $R_0 = 2\,E_0^+/3$ is the only positive $r > 0$ with $P^+(r) \geq 0$, and the orbit of the Newtonian equation's solution is a circle with radius R_0, which is revolved with constant angular velocity $\sqrt{1/R_0}$. In the second case $D^+ < 0$, the polynomial $P^+(r)$ has the three simple real roots

$$R_k \;=\; \tfrac{2}{3}\,E_0^+\,\cos(\gamma + (k-1)\tfrac{2\pi}{3}) + \tfrac{1}{3}\,E_0^+\,, \qquad k = 1,2,3$$

with $\gamma = \frac{1}{3}\arccos(1 - \frac{27}{4}\,M_0^2\,(E_0^+)^{-3})$. Since $E_0^+ > 0$ is positive and $\gamma \in]0, \pi/3[$, we have $R_2 < 0 < R_3 < 2\,E_0^+/3 < R_1 < E_0^+$, and the solution's radius $|q(t)| = r(t)$ stays in $[R_3, R_1]$ for all times $t \in \mathbb{R}$. For times t_j with $r(t_j) = R_j$, $j \in \{1,3\}$, the radial velocity equals zero and changes sign, since $\ddot{r}(t_j) = -(\frac{d}{dr}V^+)(R_j) = \frac{1}{2}\,(\frac{d}{dr}P^+)(R_j)\,R_j^{-2} \neq 0$. The radial period is given by

$$2\int_{R_3}^{R_1} \frac{x\,dx}{\sqrt{P^+(x)}} \;<\; \infty\,,$$

while the monotonicity of the angular variable φ follows from $\dot{\varphi} = M_0\,r^{-2}$. □

Remark 11 From Lemma 8 we immediately deduce, that the closed circular orbits of the Hamiltonian flow Φ_+^t are in exact correspondence with the submanifold

$$S_{cl} \;=\; \big\{(q,p) \in \mathbb{R}^4 \mid q \cdot p = 0\,,\; |q| = |p|^2\big\}\,.$$

◇

Looking for other periodic orbits than the circles, which are revolvd with constant angular velocity, we study the angle between successive pericenters (minimal distance to the origin) and apocenters (maximal distance to the origin),

$$\Phi \;=\; M_0\int_{R_3}^{R_1} \frac{dx}{x\sqrt{P^+(x)}}\,.$$

To analyse this elliptic integral we write $P^+(x)$ as a product of sums of squares, see Chapter 22.7 in [WhWa]. The ansatz is $P^+(x) = S_1(x)S_2(x)$ with $S_1(x) = -2(x - R_1)$ and $S_2(x) = (x - R_2)(x - R_3)$, where the roots R_j have been given explicitly in the proof of Lemma 8. Now, we are looking for $\lambda \in \mathbb{R}$, such that the polynomial $S_1(x) - \lambda S_2(x)$ has a repeated root. This is the case, if

$$(\lambda\,(R_2 + R_3) - 2)^2 + 4\lambda\,(2\,R_1 - \lambda\,R_2\,R_3) = 0\,,$$

that is, if

$$\lambda_{1,2} = -\frac{3\,(\cos\gamma \pm w(\gamma))}{E_0^+\,\sin^2\gamma}\,,$$

where

$$w(\gamma) = \sqrt{1 - \tfrac{4}{3}\,\sin^2\gamma}\ \in\,]0,1[\,.$$

By construction of $\lambda_{1,2}$, there exist $\alpha, \beta \in \mathbb{R}$ such that

$$S_1(x) - \lambda_1\,S_2(x) \;=\; -\lambda_1\,(x-\alpha)^2\,, \quad S_1(x) - \lambda_2\,S_2(x) \;=\; -\lambda_2\,(x-\beta)^2\,.$$

Using Matlab's symbolic toolbox once more, we obtain

$$\alpha\,,\beta \;=\; \tfrac{1}{3}\,E_0^+\,(2\cos\gamma + 1 \mp 3\,w(\gamma))\;.$$

We get the desired factorization

$$P^+(x) \;=\; \prod_{j=1,2}\left(A_j\,(x-\alpha)^2 + B_j\,(x-\beta)^2\right)$$

with $A_1, B_1 \;=\; \mp(2\,E_0^+\,w(\gamma))^{-1}$ and $A_2, B_2 \;=\; \pm\,(4\,\cos\gamma - 1)/(6\,w(\gamma)) + \frac{1}{2}$. Now, we put hands on Φ itself. If we define $f(x) = \frac{x-\alpha}{x-\beta}$ and substitute $t = f(x)$, then

$$\Phi \;=\; \frac{M_0}{\beta(\beta-\alpha)}\int_z^1 \frac{(t+1)\,dt}{(t+\frac{\alpha}{\beta})\sqrt{\prod_{j=1,2}(A_j\,t^2 + B_j)}}$$

with $z = -f(R_3) \in \mathbb{R}$. Multiplying with $t - \frac{\alpha}{\beta}$, we get

$$\begin{aligned}
\Phi \;&=\; \frac{M_0}{\beta(\beta-\alpha)}\int_z^1 \frac{(t^2 - \frac{\alpha}{\beta})\,dt}{(t^2 - \frac{\alpha^2}{\beta^2})\sqrt{\prod_{j=1,2}(A_j\,t^2 + B_j)}} \\
&\qquad + \frac{M_0}{\beta^2}\int_z^1 \frac{t\,dt}{(t^2 - \frac{\alpha^2}{\beta^2})\sqrt{\prod_{j=1,2}(A_j\,t^2 + B_j)}} \\
&=\; \frac{M_0}{\beta(\beta-\alpha)}\int_z^1 \frac{dt}{\sqrt{\prod_{j=1,2}(A_j\,t^2 + B_j)}} \\
&\quad + \frac{M_0}{\alpha\beta}\int_z^1 \frac{dt}{(1 - N\,t^2)\sqrt{\prod_{j=1,2}(A_j\,t^2 + B_j)}} + \frac{M_0}{2\beta^2}\int_{z^2}^1 \frac{dt}{(t - \frac{1}{N})\sqrt{\prod_{j=1,2}(A_j\,t + B_j)}}\,,
\end{aligned}$$

where $N = \frac{\beta^2}{\alpha^2}$. Using $1/N = 1 - 1/A_2$ for the third summand, we finally have

$$\begin{aligned} \Phi &= \frac{M_0}{\beta\sqrt{B_1\,B_2}}\left(\frac{F(1,k)-F(z,k)}{\beta-\alpha} + \frac{1}{\alpha}\left(\Pi(1,N,k)-\Pi(z,N,k)\right)\right) \\ &\quad + \frac{M_0}{2\beta^2}\sqrt{\frac{A_2}{A_1}\left(1-\frac{1}{A_2\,z^2+B_2}\right)}\,, \end{aligned}$$

with $k = \sqrt{-A_2/B_2}$. $F(\cdot,k)$ and $\Pi(\cdot,N,k)$ denote the elliptic integral of the first and third kind, respectively,

$$\begin{aligned} F(x,k) &= \int_0^x \frac{dt}{\sqrt{(1-t^2)(1-k^2\,t^2)}}\,, \\ \Pi(x,N,k) &= \int_0^x \frac{dt}{(1-N\,t^2)\sqrt{(1-t^2)(1-k^2\,t^2)}}\,. \end{aligned}$$

The preceding calculation shold have erased any hope to obtain additional meaningful information on the classical dynamics associated with the upper electronic level.

Lemma 9 (Lower Electronic Level) *The solution of the Newtonian equation of motion*

$$\ddot{q}(t) = \tfrac{q(t)}{|q(t)|}\,, \qquad q(0) = q_0\,, \qquad \dot{q}(0) = p_0$$

with initial datum $(q_0, p_0) \in \mathbb{R}^4$ *of non-zero angular momentum* $M_0 = q_0 \wedge p_0 \neq 0$ *satisfies for all times* $t \in \mathbb{R}$

$$|\,q(t)\,| \geq r_*\,,$$

where $r_* > 0$ *is the unique positive root of the polynomial* $P^-(r) = 2\,r^3 + 2\,E_0^-\,r^2 - M_0^2$ *with* $E_0^- = \frac{1}{2}|p_0|^2 - |q_0|$. *Moreover,* $|q(t)| \to \infty$ *as* $t \to \pm\infty$.

Proof. The polynomial $P^-(r)$ decreases monotonously inbetween zero and $-2\,E_0^-/3$ and increases monotonously outside this interval. If $E_0^- \leq 0$, then the discriminant $D^- = \frac{1}{2}\,M_0^2\left(\frac{1}{8}\,M_0^2 - \frac{1}{27}\,(E_0^-)^3\right) > 0$ is positive. We have roots $a \in \mathbb{R}$ and $c \in \mathbb{C}\setminus\mathbb{R}$ with $P^-(r) = 2\,(r-a)(r-c)(r-\bar{c})$. Since $-2\,a\,|c|^2 = -M_0^2$, we have $a > 0$. Moreover, $2\,(a\,\mathrm{Re}(c)+|c|^2) = 0$, which gives $\mathrm{Re}(c) < 0$. Since $-2(a + \mathrm{Re}(c)) = 2\,E_0^-$, we also have $a = -E_0^- - \mathrm{Re}(c) > -2\,E_0^-/3$. Thus, $P^-(r)$ is monotonically increasing around a, and $P^-(r) \geq 0$ if and only if $r \geq a$. Next, we assume $E_0^- > 0$. We factorize $P^-(r) = 2(r-a)(r-b_1)(r-b_2)$ with $a \in \mathbb{R}$ and $b_1, b_2 \in \mathbb{C}$. If $b_1 = \overline{b_2} \in \mathbb{C}\setminus\mathbb{R}$, then $a > 0$, and $P^-(r) \geq 0$ if and only if $r \geq a$. If $b_1, b_2 \in \mathbb{R}$, $b_1 \neq b_2$, then $P^-(r)$ has three real simple roots, exactly one of them being positive. Thus, without loss of generality $a > 0$, and the only positive r with $P^-(r) \geq 0$ are the r with $r \geq a$. If $b_1 = b_2 \in \mathbb{R}$, then $b_1 = -2\,E_0^-/3$, and the only positive r with $p(r) \geq 0$ are again the r with $r \geq a$. Therefore, independently from the energy's or determinant's sign, the Newtonian motion stays outside the disc, whose radius r_* is the the only positive root of $P^-(r)$. If $D^- = 0$, that is if $27\,M_0^2 = 8\,(E_0^-)^3$, then $r_* = E_0^-/3$. If $D^- < 0$, then

$$r_* = \tfrac{2}{3}\,E_0^-\,\cos\!\left(\tfrac{1}{3}\arccos\!\left(\tfrac{27}{4}M_0^2\,(E_0^-)^3 - 1\right)\right) - \tfrac{1}{3}\,E_0^-\,,$$

which lies in the interval $]0, E_0^-/3[$. If $D^- > 0$, then $r_* = u + (E_0^-)^2/(9u)$ with $u = (\frac{1}{4} M_0^2 - \frac{1}{27}(E_0^-)^3 + \sqrt{D^-})^{1/3}$. Since the function $u \mapsto u + (E_0^-)^2/(9u)$ attains its minimum for $u = E_0^-/3$, we have $r_* > E_0^-/3$. If $r_0 = r(0)$, then for all $R > r_*$ the integral

$$\int_{r_0}^{R} \frac{x\,dx}{\sqrt{P^-(x)}} < \infty$$

exists and is finite. Hence, every $R > r_*$ can be reached within finite time, and we have $r(t) \to \infty$ as $t \to \infty$. □

Summarizing all the preceding details, we have seen different types of classical motion for the two Newtonian equations (35). Related to the upper electronic level E^+, there is constraint motion. Especially, there exist periodic orbits, which are circles revolved with constant angular velocity. For the lower electronic level E^-, the motion is unbounded.

Part C

An Asymptotic Semigroup

10 Propagation Near the Crossing

It is expected, that near the crossing the solution $\psi^\varepsilon(t) = e^{-iH^\varepsilon t/\varepsilon}\psi_0^\varepsilon$ of our model system (1) exhibits leadig order non-adiabatic transitions between the subspaces $\mathrm{Ran}\Pi_+$ and $\mathrm{Ran}\Pi_-$ for a large class of initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. It is our goal now to modify the transport equation (34) associated with the group $\mathcal{L}_0^t$ by taking transfer between the diagonal components $(w_+^\varepsilon(t), w_-^\varepsilon(t))$ of the Wigner function into account.

Following an observation by L. Nédélec [Ne], we will show in Section 15 of Part D, that our model Hamiltonian $H^\varepsilon = -\frac{\varepsilon^2}{2}\Delta_q + V(q)$ is unitarily equivalent to the semi-classical Weyl quantization of

$$\tfrac{1}{2}|p|^2 + |p|^{-1}\begin{pmatrix} q\cdot p & q\wedge p \\ q\wedge p & -q\cdot p \end{pmatrix}. \tag{37}$$

The symbol in (37) carries two key signatures of the classical dynamics studied in the previous section: the angular momentum $q \wedge p$, which is preserved by the Hamiltonian flows $\Phi_\pm^t$, and the function $q \cdot p$, which characterizes the hypersurface

$$S = \{(q,p) \in \mathbb{R}^4 \mid q \cdot p = 0\}$$

containing the points in phase space, at which the classical trajectories attain their minimal distance to the crossing manifold $\{q = 0\}$, cf. Figure 7.

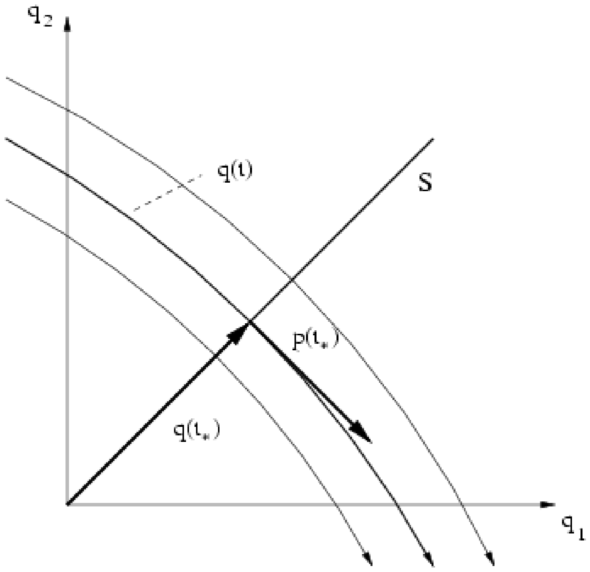


Figure 7: We see the projections of three neighboring trajectories $(q(t), p(t))$ onto configuration space $\mathbb{R}^2_q$. The crossing manifold $\{q = 0\}$ is therefore projected onto the origin. The trajectories attain their minimal distance to the crossing at the time t_* when $q(t_*)\cdot p(t_*) = 0$. The points in phase space where $q \cdot p = 0$ build up the jump manifold S.

The underlying heuristic picture for the dynamics near the crossing is to replace (q,p) in (37) by classical trajectories $(q(t), p(t))$ related to the classical flows $\Phi_\pm^t$ and to solve the purely time-adiabatic problem

$$i\varepsilon\partial_t\,\phi(t) \;=\; |p(t)|^{-1}\begin{pmatrix} q(t)\cdot p(t) & q(t)\wedge p(t) \\ q(t)\wedge p(t) & -q(t)\cdot p(t)\end{pmatrix}\phi(t)\,, \qquad \phi(t)\in\mathbb{C}^2\,. \tag{38}$$

Since the leading order transitions happen only in the region where a trajectory has minimal distance to the crossing, we linearize the flows around S. The linearizations of the classical flows $\Phi^t_\pm$ at a point $(q_*, p_*)\in S$ are

$$q^\pm(t) = q_* + t\,p_* + \mathcal{O}(t^2) \qquad \text{and} \qquad p^\pm(t) = p_* \mp t\,q_*/|q_*| + \mathcal{O}(t^2)\,. \tag{39}$$

The system (38) becomes

$$\underbrace{i\,\tfrac{\varepsilon}{|p_*|}}_{=:\,\widetilde{\varepsilon}}\,\partial_t\,\phi(t) = \begin{pmatrix} t & \frac{q_*\wedge p_*}{|p_*|^2} \\ \frac{q_*\wedge p_*}{|p_*|^2} & -t\end{pmatrix}\phi(t) =: \begin{pmatrix} t & \delta \\ \delta & -t\end{pmatrix}\phi(t)\,, \tag{40}$$

where we used that $|q_*|/|p_*|^2 \ll 1$ near the crossing. We note, that the purely time-dependent system (40) does not depend on whether we employ Φ^t_+ or Φ^t_- for its formal derivation. However, (40) is nothing but the famous Landau-Zener problem. The time-dependent matrix

$$H_\delta(t) \;:=\; \begin{pmatrix} t & \delta \\ \delta & -t\end{pmatrix}$$

has the eigenvalues $\pm\sqrt{t^2+\delta^2}$, which attain their minimal distance 2δ for $t = 0$. Already in 1932, C. Zener [Ze] considers the ordinary differential system (40) for initial conditions of the form

$$\phi(-\infty) \;=\; \phi^+(-\infty)\,e^+(-\infty)\,, \qquad |\phi^+(-\infty)| \;=\; 1\,,$$

where $e^\pm(\cdot)\in C^\infty(\mathbb{R},\mathbb{C}^2)$ denote smooth eigenfunctions of the matrix $H_\delta(\cdot)$. He derives a Weber equation and obtains by its asymptotic analysis, that the large time behaviour of the solution $\phi(t)$ is given as

$$\phi(\infty) \;=\; \phi^+(\infty)\,e^+(\infty) \;+\; \phi^-(\infty)\,e^-(\infty)$$

with

$$|\phi^-(\infty)|^2 \;+\; |\phi^+(\infty)|^2 \;=\; 1\,, \qquad |\phi^-(\infty)|^2 \;=\; \exp\big(-\pi\delta^2/\widetilde{\varepsilon}\big) \;=:\; P^{\widetilde{\varepsilon}}_\delta\,.$$

Due to the problem's symmetry, the same transition rate $P^{\widetilde{\varepsilon}}_\delta$ also applies, when only the lower level is occupied for $t\to-\infty$. Summarizing, for initial data of the form

$$\begin{pmatrix} |\phi^+(-\infty)|^2 \\ |\phi^-(-\infty)|^2\end{pmatrix} = \begin{pmatrix} 1 \\ 0\end{pmatrix} \qquad \text{or} \qquad \begin{pmatrix} |\phi^+(-\infty)|^2 \\ |\phi^-(-\infty)|^2\end{pmatrix} = \begin{pmatrix} 0 \\ 1\end{pmatrix}$$

the non-adiabatic transitions for the solution $\phi(t)$ of (40) can be expressed as

$$\begin{pmatrix} |\phi^+(\infty)|^2 \\ |\phi^-(\infty)|^2\end{pmatrix} = \begin{pmatrix} 1-P^{\widetilde{\varepsilon}}_\delta & P^{\widetilde{\varepsilon}}_\delta \\ P^{\widetilde{\varepsilon}}_\delta & 1-P^{\widetilde{\varepsilon}}_\delta\end{pmatrix}\begin{pmatrix} |\phi^+(-\infty)|^2 \\ |\phi^-(-\infty)|^2\end{pmatrix},$$

and we see, that for the ordinary differential problem the probability of a non-adiabatic transition $P_\delta^{\tilde\varepsilon} = \exp(-\pi\,\delta\,/\,\tilde\varepsilon)$ is the larger the smaller the minimal gap δ and the smaller the smaller the adiabatic parameter $\tilde\varepsilon$. While C. Zener has studied the special linear problem (40), it is L. Landau's work on non-adiabatic transitions induced by atomic collisions [La], which has given the transition probability $P_\delta^{\tilde\varepsilon}$ the name *Landau-Zener formula.* For more information on purely time-dependent Landau-Zener type problems we refer to the review [JoPf]. Re-identifying the parameters $\delta = |p_*|^{-2}\, q_* \wedge p_*$ and $\tilde\varepsilon = |p_*|^{-1}\varepsilon$, the rate $P_\delta^{\tilde\varepsilon}$ reads in the conical crossing setting as

$$T^\varepsilon(q_*, p_*) \;:=\; \exp\left(-\frac{\pi}{\varepsilon}\,\frac{(q_* \wedge p_*)^2}{|p_*|^3}\right) \;=\; \exp\left(-\frac{\pi}{\varepsilon}\,\frac{|q_*|^2}{|p_*|}\right)\,. \tag{41}$$

Here, the transition probability $T^\varepsilon(q_*, p_*)$ depends on three factors: the angular momentum $q_* \wedge p_*$, the momentum strength $|p_*|$, and the semi-classical parameter ε. Clearly, the transition rate $T^\varepsilon(q_*, p_*)$ is the larger the smaller the angular momentum $q_* \wedge p*$, the larger the momentum strength $|p_*|$, and the larger the semi-classical parameter ε.

Trajectories with $|p_*|$ of order one and $q_* \wedge p_*$ of order $\sqrt{\varepsilon}$ induce leading order non-adiabatic transitions.

It is the goal of the subsequent analysis to show, that the heuristic picture of classical transport in combination with the transition probability (41) yields a correct description of the leading order dynamics.

Remark 12 The heuristic argument yielding the Landau-Zener formula (41) also applies to the generic potential discussed in Section 3.1 of Part A

$$V(q) \;=\; \begin{pmatrix} a\cdot q & b\cdot q \\ b\cdot q & -a\cdot q \end{pmatrix}.$$

If we denote by $M = (a^t, b^t)$ the 2×2-matrix with row vectors $a^t, b^t \in \mathbb{R}^2$, then the jump manifold is given by $\{(q,p) \in \mathbb{R}^4 \mid Mq \cdot Mp = 0\}$, and the transition probability reads as

$$T_\varepsilon(q_*, p_*) \;=\; \exp\left(-\frac{\pi}{\varepsilon}\frac{(Mq_* \wedge Mp_*)^2}{|Mp_*|^3}\right)\,.$$

$\diamondsuit$

11 A Markov Process

To incorporate the ε-dependent transition probability (41) into the transport of the Wigner function, we first append to phase space a label $j \in \{-1, 1\}$ indicating, whether the description refers to $\mathrm{Ran}\Pi^-$ or $\mathrm{Ran}\Pi^+$. We define a family of random trajectories

$$\mathcal{J}_\varepsilon^{(q,p,j)} : \;[0,\infty) \to \mathbb{R}^4 \times \{-1, 1\}\,,$$

where $\mathcal{J}_\varepsilon^{(q,p,j)}(t) = (\Phi_j^t(q,p), j)$ as long as $q^j(t)\cdot p^j(t) \neq 0$. Whenever the deterministic flow $\Phi_j^t(q,p)$ hits the manifold $S = \{(q,p) \in \mathbb{R}^4 \mid q\cdot p = 0\}$ a jump occurs with probability $T^\varepsilon(q,p)$, i.e. j changes to $-j$ with probability $T^\varepsilon(q,p)$. After the jump the trajectory follows again the deterministic flow depending on j until the trajectory hits again S. At the jump hypersurface S, the trajectories are chosen right continuous. On the submanifold $S_{cl} = \{(q,p) \in S \mid |p|^2 = |q|\}$ of closed circular orbits of Φ_+^t the trajectories do not jump.

Remark 13 In each finite time interval $[0,T] \subset [0,\infty[$ each path $(q,p,j) \to \mathcal{J}_\varepsilon^{(q,p,j)}(t)$ has only a finite number of jumps and remains in a bounded region of phase space. Moreover, the paths $(q,p,j) \to \mathcal{J}_\varepsilon^{(q,p,j)}(t)$ are smooth away from S, i.e. on $(\mathbb{R}^4 \setminus S) \times \{-1,1\}$. $\diamondsuit$

The random trajectories $\mathcal{J}_\varepsilon^{(q,p,j)}$ define a Markov process

$$\left\{ X_\varepsilon^{(q,p,j)} \mid (q,p,j) \in \mathbb{R}^4 \times \{-1,1\} \right\}$$

on $\mathbb{R}^4 \times \{-1,1\}$, see for example III-§1 in [Dy]. This Markov process combines deterministic transport on the energy levels with jumps inbetween them according to the Landau-Zener rate, whenever a trajectory attains its minimal distance. Since the trajectories $\mathcal{J}_\varepsilon^{(q,p,j)}(t)$ are defined for all $t \in [0,\infty[$ the process is non-terminating.

Remark 14 We emphasize, that the underlying physics is of course not one of instantaneously jumping particles. Indeed, for the purely time-dependent problem (40) it is known that the non-adiabatic transition occurs smoothly within an $\sqrt{\varepsilon}$-neighborhood of $t=0$, see [HaJo, BeTe]. $\diamondsuit$

The transition function $\mathbb{P}_\varepsilon((q,p,j);t,\Gamma)$ of the Markov process gives the probability of being at time $t \geq 0$ in the measurable set $\Gamma \subset \mathbb{R}^4 \times \{-1,1\}$ having started in the state (q,p,j). With the transition function one associates a backwards and a forwards semigroup, which act on function spaces respectively spaces of set functions, see II-§1 in [Dy] or Chapter I in [Li]. The backwards semigroup $\mathcal{L}_\varepsilon^t$ acting on bounded measurable functions $f : \mathbb{R}^4 \times \{-1,1\} \to \mathbb{C}$ is defined via

$$(\mathcal{L}_\varepsilon^t f)(q,p,j) \;:=\; \mathbb{E}_\varepsilon^{(q,p,j)} f(\,\mathcal{J}_\varepsilon^{(q,p,j)}(t)\,) \;=\; \int_{\mathbb{R}^4\times\{-1,1\}} f(x,\xi,k)\,\mathbb{P}_\varepsilon((q,p,j);t,d(x,\xi,k))\;.$$

For our purposes, it will be enough to work with functions, which are continuous away from the jump manifold S and satisfy a suitable inflow and outflow condition at S.

Definition 7 A compactly supported function $f \in C_c((\mathbb{R}^4 \setminus S) \times \{-1,1\}, \mathbb{C})$ belongs to the space $\mathcal{C}$, if it satisfies the following boundary conditions at $(S \setminus S_{cl}) \times \{-1,1\}$:

$$\begin{aligned}\lim_{\delta\to+0} f(q-\delta p, p+\delta j q/|q|, j) &= T^\varepsilon(q,p)\lim_{\delta\to+0} f(q+\delta p, p+\delta j q/|q|, -j)\\ &= T^\varepsilon(q,p)\, f(q,p,-j)\end{aligned}$$

and

$$\begin{aligned}\lim_{\delta\to+0} f(q-\delta p, p+\delta j q/|q|, j) &= (1-T^\varepsilon(q,p))\lim_{\delta\to+0} f(q+\delta p, p-\delta j q/|q|, j)\\ &= (1-T^\varepsilon(q,p))\, f(q,p,j)\,.\end{aligned}$$

REMARK 15 The limits in the preceding definition are taken along the linearization of the unique trajectory of the Hamiltonian system (32) passing through a point in $S \setminus S_{cl}$ before respectively after hitting the jump manifold S, see also (39). $\diamondsuit$

By construction of the function space $\mathcal{C}$, the semigroup $\mathcal{L}_\varepsilon^t$ leaves $\mathcal{C}$ invariant, that is

$$\mathcal{L}_\varepsilon^t : \mathcal{C} \to \mathcal{C}, \qquad t \in [0, \infty[.$$

We write continuous matrix-valued functions $a \in C_c(\mathbb{R}^4 \setminus S, \mathcal{L}(\mathbb{C}^2))$ as

$$a = a^+\Pi^+ + a^-\Pi^- + \Pi^+ a \Pi^- + \Pi^- a \Pi^+$$

with $a^\pm := \mathrm{tr}(a\,\Pi^\pm)$. We denote by $\mathcal{C}_{\mathrm{diag}}$ the space of functions $a \in C_c(\mathbb{R}^4 \setminus S, \mathcal{L}(\mathbb{C}^2))$ such that $a = a^+\Pi^+ + a^-\Pi^-$ with $a^+, a^- \in \mathcal{C}$, and set for $a \in \mathcal{C}_{\mathrm{diag}}$

$$\mathcal{L}_{\varepsilon,\pm}^t a := \left(\mathcal{L}_\varepsilon^t(a^+, a^-)\right)^\pm, \qquad \mathcal{L}_\varepsilon^t a := \left(\mathcal{L}_{\varepsilon,+}^t a\right)\Pi^+ + \left(\mathcal{L}_{\varepsilon,-}^t a\right)\Pi^-.$$

With this definition the semigroup $\mathcal{L}_\varepsilon^t$ acts invariantly on $\mathcal{C}_{\mathrm{diag}}$, and we can now define its action on Wigner functions by duality.

DEFINITION 8 Let $W^\varepsilon(\psi)$ be the Wigner function of some wave function $\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. We define $\mathcal{L}_\varepsilon^t W^\varepsilon(\psi)$ as the linear functional

$$\mathcal{L}_\varepsilon^t W^\varepsilon(\psi) : \quad \mathcal{C}_{\mathrm{diag}} \to \mathbb{C}, \quad a \mapsto \int_{\mathbb{R}^4} \mathrm{tr}\left(W^\varepsilon(\psi)(q,p)\left(\mathcal{L}_\varepsilon^t a\right)(q,p)\right) dq\, dp.$$

Since the Wigner function $W^\varepsilon(\psi) \in C_0(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$ is continuous and $\mathcal{L}_\varepsilon^t a \in \mathcal{C}_{\mathrm{diag}}$, we clearly have $\mathcal{L}_\varepsilon^t W^\varepsilon(\psi) \in C(\mathbb{R}^4 \setminus S, \mathcal{L}(\mathbb{C}^2))$. Moreover, $S \subset \mathbb{R}^4$ has zero Lebesgue measure. Hence,

$$\mathcal{L}_\varepsilon^t W^\varepsilon(\psi) \in L^1_{\mathrm{loc}}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2)).$$

Analogously to the Born-Oppenheimer function $W_{\mathrm{BO}}^\varepsilon(t)$ defined in Section 9.2 of Part B, we name

$$W_{\mathrm{LZ}}^\varepsilon(t) := \mathcal{L}_\varepsilon^t W^\varepsilon(\psi_0) \in L^1_{\mathrm{loc}}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2)), \qquad t \in [0, \infty[$$

the Landau-Zener function of an initial datum $\psi_0 \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. The function $W_{\mathrm{LZ}}^\varepsilon(t)$ incorporates classical transport and ε-dependent non-adiabatic transitions at the jump manifold S. Clearly, the semigroup $\mathcal{L}_\varepsilon^t$ and consequently $W_{\mathrm{LZ}}^\varepsilon(t)$ do not correctly resolve the dynamics directly at the jump manifold S, but give an approximate description of the total non-adiabatic transfer, when the solution has passed by. Hence, the Landau-Zener function $W_{\mathrm{LZ}}^\varepsilon(t)$ can only be a sensible approximation to the true Wigner function $W^\varepsilon(\psi^\varepsilon(t))$ away from S. Therefore we restrict ourselves to test functions supported away from S and we also have to assume that the initial data have negligible mass near the jump manifold S.

DEFINITION 9 (NEGLIGIBLE MASS) A sequence of wave functions $(\psi^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^2, \mathbb{C}^2)$ is said to have *negligible mass* near the jump manifold S, if there exists $\delta > 0$ such that

$$\lim_{\varepsilon \to 0} \int_{S_\delta} |W^\varepsilon(\psi_0^\varepsilon)(q,p)|\, dq\, dp = 0$$

with $S_\delta = \{(q,p) \in \mathbb{R}^4 \mid |q \cdot p| \leq \delta\}$ the closed δ-tube around S.

Initial data with negligible mass near S are, for example, associated with semi-classical Gaussians $(g^\varepsilon)_{\varepsilon>0}$ or WKB type functions $(\omega^\varepsilon)_{\varepsilon>0}$ as defined in (2) respectively (23). The center $(q_0, p_0) \in \mathbb{R}^4$ of the Gaussians must not lie not on S, that is $q_0 \cdot p_0 \neq 0$. For points $q \in \mathrm{supp}(a)$ in the support of the WKB function's amplitude one needs $q \cdot \nabla f(q) \neq 0$.

Though incorporating non-adiabatic transitions, the semigroup $\mathcal{L}_\varepsilon^t$ still gives a semi-classical description of the dynamics. Hence, we do not obtain information about the off-diagonal terms of the Wigner function, which are highly oscillatory and vanish when averaged over time, see Lemma 11 later on. By choosing observables, which are diagonal with respect to the potential $V(q)$, we conveniently suppress the uncontrolled off-diagonal parts of $W^\varepsilon(\psi^\varepsilon(t))$. This restriction to the diagonal components, however, prohibits the resolution of possible *interferences* between parts of the wave function originating from different levels. Such interferences might occur if classical trajectories arrive with the same momentum at the same time at the jump manifold on the upper and the lower band. A simple condition ruling out such a scenario is the choice of initial data just associated with $\mathrm{Ran}\Pi^+$, that is $\psi_0^\varepsilon(q) = \psi_{0,+}^\varepsilon(q)\,\chi^+(q)$ with $\psi_{0,+}^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C})$. In this case, all trajectories associated with the flow Φ_-^t originate from trajectories of the flow Φ_+^t having passed the jump manifold S. Since such trajectories $(q^-(t), p^-(t))$ do not come back to S, there are no interferences.

The last issue to be addressed before formulating the theorem for the Landau-Zener function $W_{\mathrm{LZ}}^\varepsilon(t)$ is rather technical and will impose cumbersome analysis on us in the following. Since we must allow for ε-dependent initial data, we have to make sure that the family of initial wave functions $(\psi_0^\varepsilon)_{\varepsilon>0}$ behaves properly as $\varepsilon \to 0$. It turns out that the appropriate condition is that the sequence of two-scale Wigner functionals $(W_2^\varepsilon(\psi_0^\varepsilon))_{\varepsilon>0}$ converges to a two-scale Wigner measure ρ_0. We postpone the definition and discussion of two-scale Wigner functionals and measures to the following Section 12. However, we note that this assumption is satisfied by all standard families of initial wave functions $(\psi_0^\varepsilon)_{\varepsilon>0}$ like semi-classical Gaussians or WKB states and also by initial conditions not depending on ε at all. Moreover, the assumption can be dropped completely, if one is willing to work with subsequences of the initial sequence $(\psi_0^\varepsilon)_{\varepsilon>0}$.

THEOREM 8 (L. & TEUFEL) *Let $(\psi_0^\varepsilon)_{\varepsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^2, \mathbb{C}^2)$ associated with $\mathrm{Ran}\Pi^+$, that is with $w_-^\varepsilon(\psi_0^\varepsilon) = 0$, with negligible mass near the jump manifold S. Assume that the sequence of two-scale Wigner functionals $(W_2^\varepsilon(\psi_0^\varepsilon))_{\varepsilon>0}$ has a weak*-limit ρ_0 as to be defined in Definition 11 later on.*

Then, for all $T > 0$ the solution $\psi^\varepsilon(t)$ of the Schrödinger equation (1) with initial data $\psi^\varepsilon(0) = \psi_0^\varepsilon$ satisfies

$$\lim_{\varepsilon \to 0} \sup_{t \in [0,T]} \int_{\mathbb{R}^4} \mathrm{tr}\Big(\big(W^\varepsilon(\psi^\varepsilon(t)) - W_{\mathrm{LZ}}^\varepsilon(t)\big)(q,p)\, a(q,p) \Big)\, dq\, dp \;=\; 0 \tag{42}$$

for all $a \in C_c^\infty(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$ with $\mathrm{supp}(a) \subset \mathbb{R}^4 \setminus S$ and $[a(q,p), V(q)] = 0$ for $(q,p) \in \mathbb{R}^4$.

The proof of Theorem 8 will be given in Section 13. Before starting the preparations for this undertaking, we emphasize that Theorem 8 extends the Born-Oppenheimer approximation in a non-trivial way. The transition probabilities $T^\varepsilon(q,p)$ incorporated into the semigroup

$\mathcal{L}_\varepsilon^t$ result in leading order non-adiabatic transitions for a large class of initial data. All initial wave functions with phase space support in an $\sqrt{\varepsilon}$-neighborhood of the hypersurface of zero angular momentum $\{(q,p) \in \mathbb{R}^4 \mid q \wedge p = 0\}$ exhibit order one transitions.

12 Two-Scale Wigner Functionals and Measures

In this section we provide a self-contained discussion of the necessary two-scale analysis required for the proof of Theorem 8. Two-scale Wigner measures are measures on an extended phase space $\mathbb{R}^{2d} \times \mathbb{R}_\eta$, using the extra variable $\eta \in \mathbb{R}$ to resolve concentration effects on certain submanifolds of phase space on the coarser scale $\sqrt{\varepsilon}$. They have been introduced by C. Fermanian-Kammerer [Fe] and L. Miller [Mil] for the analysis of propagation through shock hypersurfaces and sharp interfaces. In this section, we review and extend a number of notions and results from [FeGe1], which we then will use in the proof of Theorem 8. In particular, we pursuit three issues. Firstly, we present a self-contained construction of two-scale measures, which just relies on the Calderón-Vaillancourt Theorem and a two-scale version of the sharp Gårding inequality. Secondly, the two-scale Wigner measures used in [FeGe1] are measures on an extended phase space of space-time $T^*(\mathbb{R}_t \times \mathbb{R}^2_q) \times \mathbb{R}_\eta = \mathbb{R}^7$. Here, we provide a detailed discussion of the necessary tools to incorporate their Landau-Zener type formula into a description, which is pointwise in time. Thirdly, the space of observables used in [FeGe1] consists of functions, which are constant for large values of the additional coordinate η. That space is not invariant under multiplication by the two-scale transition rate $\exp(-\pi\eta^2/|p|^3)$, and we have to enlarge the space of admissible observables to obtain a well-defined description of the dynamics by means of a semigroup.

12.1 Two-Scale Wigner Functionals

We want to analyze concentration effects with respect to a submanifold in phase space

$$I_g \;:=\; \left\{(q,p) \in \mathbb{R}^4 \mid g(q,p) = 0\right\}.$$

For the Schrödinger equation (1), we will choose $g(q,p) = q \wedge p$, which is angular momentum, a conserved quantity under the associated Hamiltonian dynamics. We recall, that $q \wedge p$ also appeared explicitly in the Landau-Zener transition rate (41). This rate indicates, that only trajectories within a $\sqrt{\varepsilon}$-neighborhood of I_g in phase space, i.e. in a set

$$\left\{(q,p) \in \mathbb{R}^4 \mid \; |q \wedge p| \;\leq\; \text{const.}\sqrt{\varepsilon}\;\right\},$$

experience order one transition probabilities when coming close to the crossing. The Wigner measure, however, does not resolve this $\sqrt{\varepsilon}$-neighborhood, and a more detailed two-scale analysis becomes necessary. For the general statements about two-scale Wigner functionals and measures, we only assume that $g \in C^\infty(\mathbb{R}^4,\mathbb{R})$ is a smooth polynomially bounded function, that is for all $\beta \in \mathbb{N}_0^4$ there is a positive constant $C = C(\beta) > 0$ and a natural number $M = M(\beta) \in \mathbb{N}_0$ such that

$$\forall (q,p) \in \mathbb{R}^4 : \; |\partial^\beta g(q,p)| \;\leq\; C\,\langle (q,p)\rangle^M.$$

The function g provides us with a notion of (signed) distance to the manifold I_g through $d((q,p), I_g) = g(q,p)$. In the following, the variable $\eta \in \overline{\mathbb{R}}$ measures this distance scaled with $\sqrt{\varepsilon}$, that is $\eta(q,p) = g(q,p)/\sqrt{\varepsilon}$. Since we are interested in the limit $\varepsilon \to 0$, the variable η is viewed as an element of the one-point compactification $\overline{\mathbb{R}}$ of $\mathbb{R}$. We will use observables depending on $(q,p) \in \mathbb{R}^4$ and $\eta \in \overline{\mathbb{R}}$ to test the Wigner function near I_g with respect to the $\sqrt{\varepsilon}$ scale. For $a \in C_b^\infty(\mathbb{R}^5, \mathcal{L}(\mathbb{C}^2))$ let

$$\textbf{(P)} \quad \|\langle(q,p)\rangle^\beta \partial^\gamma a(q,p,\eta)\|_\infty < \infty \text{ for all } \beta \in \mathbb{N}_0 \text{ and } \gamma \in \mathbb{N}_0^5,$$
$$\exists\, a_\infty \in C_b^\infty(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2)) : \lim_{|\eta|\to\infty} \|a(\cdot,\eta) - a_\infty\|_\infty = 0\,.$$

We define the relevant test function space as

$$\mathcal{A} := \left\{ a \in C_b^\infty(\mathbb{R}^5, \mathcal{L}(\mathbb{C}^2)) \mid a \text{ satisfies property } \textbf{(P)} \right\}$$

and equip it with the topology, which is induced by the family of semi-norms

$$\|\,\langle(q,p)\rangle^\beta\, \partial^\gamma a(q,p,\eta)\,\|_\infty\,, \qquad \beta \in \mathbb{N}_0\,,\ \gamma \in \mathbb{N}_0^5\,. \tag{43}$$

We note, that $\mathcal{A}$ is a Fréchet space with the Heine-Borel property, that is, closed and bounded sets are compact. Therefore, $\mathcal{A}$ is a Montel space. In the dual $\mathcal{A}'$ of such spaces, every weak* convergent sequence is strongly convergent, meaning that for a sequence $(l_n)_{n\in\mathbb{N}}$ in $\mathcal{A}'$

$$\forall a \in \mathcal{A}: \lim_{n\to\infty} l_n(a) = l(a) \quad \Longrightarrow \quad \forall \text{ bounded } B \subset \mathcal{A}: \lim_{n\to\infty} \sup_{a\in B} |\, l_n(a) - l(a)\,| = 0\,,$$

see for example Proposition 34.6 in [Tr]. We will use this strong convergence property later on. For $a \in \mathcal{A}$, we denote by

$$s_5(a) := \sum_{|\beta|,|\gamma|\leq 5} \|\,\langle(q,p)\rangle^\beta\, \partial^\gamma a(q,p,\eta)\,\|_\infty\,,$$

the finite sum over Schwartz norms, which are of the form (43). For observables $a \in \mathcal{A}$, the scaled function

$$(q,p) \mapsto a_\varepsilon(q,p) := a(q,p,\tfrac{g(q,p)}{\sqrt{\varepsilon}})$$

lies in the symbol class $S^0_{1/2}(1)$, and we observe that $c_4(a_\varepsilon)$ cannot be bounded by $s_5(a)$ uniformly in $\varepsilon > 0$. Therefore, as in the proof of the Calderón-Vaillancourt Theorem for symbol classes $S^0_\delta(1)$ with $\delta \in [0,1/2]$, see e.g. Theorem 7.11 in [DiSj], we use the unitary scaling

$$S^\varepsilon : L^2(\mathbb{R}^2,\mathbb{C}^2) \to L^2(\mathbb{R}^2,\mathbb{C}^2)\,, \quad \psi(q) \mapsto (S^\varepsilon\psi)(q) := \sqrt{\varepsilon}\,\psi(\sqrt{\varepsilon}q)$$

and define for $a \in \mathcal{A}$ the alternatively scaled symbol

$$(q,p) \mapsto a_{\varepsilon,2}(q,p) := a(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p, \tfrac{g(\sqrt{\varepsilon}q,\sqrt{\varepsilon}p)}{\sqrt{\varepsilon}})\,,$$

which belongs to the symbol class $S^0_0(1)$.

Lemma 10 (Rescaling) *Let $a \in \mathcal{A}$ and $\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)$. Then,*

$$\langle\psi, a_\varepsilon(q,-i\varepsilon\nabla_q)\,\psi\rangle_{L^2(\mathbb{R}^2)} = \langle S^\varepsilon\psi, a_{\varepsilon,2}(q,-i\nabla_q)\,S^\varepsilon\,\psi\rangle_{L^2(\mathbb{R}^2)}\,. \tag{44}$$

PROOF. Since a_ε and $a_{\varepsilon,2}$ are Schwartz functions, we just have to carry out an calculation. We have for $\psi \in \mathcal{S}(\mathbb{R}^2, \mathbb{C}^2)$

$$\langle \psi, a_\varepsilon(q, -i\varepsilon\nabla_q)\,\psi\rangle_{L^2(\mathbb{R}^2)} \;=\; (2\pi\varepsilon)^{-2}\int_{\mathbb{R}^6} \overline{\psi}(q)\, e^{i(q-q')\cdot p/\varepsilon}\; a_\varepsilon(\tfrac{q+q'}{2}, p)\,\psi(q')\,dq'\,dp\,dq\,.$$

Substituting $q = \sqrt{\varepsilon}x$, $q' = \sqrt{\varepsilon}x'$, and $p = \sqrt{\varepsilon}\,\xi$, we obtain

$$\begin{aligned}
&\langle \psi, a_\varepsilon(q, -i\varepsilon\nabla_q)\,\psi\rangle_{L^2(\mathbb{R}^2)}\\
&\quad= \varepsilon(2\pi)^{-2}\int_{\mathbb{R}^6} \overline{\psi}(\sqrt{\varepsilon}x)\, e^{i(x-x')\cdot\xi}\, a\big(\sqrt{\varepsilon}\,\tfrac{x+x'}{2}, \sqrt{\varepsilon}\,\xi, g(\sqrt{\varepsilon}\,\tfrac{x+x'}{2}, \sqrt{\varepsilon}\,\xi)/\sqrt{\varepsilon}\,\big)\ldots\\
&\qquad\qquad\qquad\ldots\psi(\sqrt{\varepsilon}x')\,dx'\,d\xi\,dx\\
&\quad= \langle S^\varepsilon\psi, a_{\varepsilon,2}(q, -i\nabla_q)\,S^\varepsilon\,\psi\rangle_{L^2(\mathbb{R}^2)}\;.
\end{aligned}$$

Since $a_{\varepsilon,2}(q, -i\nabla_q)$ is bounded, we can conclude (44) also for $\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ by density. □

For $a \in \mathcal{A}$ we have $c_4(a_{\varepsilon,2}) \le \text{const.}\, s_5(a)$ uniformly in $\varepsilon > 0$. Hence,

$$\mathcal{A} \to \mathbb{C}\,, \quad a \mapsto \langle S^\varepsilon\psi, a_{\varepsilon,2}(q, -i\nabla_q)\,S^\varepsilon\psi\rangle_{L^2(\mathbb{R}^2)}$$

defines a continuous linear functional on $\mathcal{A}$.

DEFINITION 10 (TWO-SCALE WIGNER FUNCTIONAL) Let $\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. The continuous linear functional

$$W_2^\varepsilon(\psi):\quad \mathcal{A} \to \mathbb{C}\,,\quad a \mapsto \langle W_2^\varepsilon(\psi), a\rangle_{\mathcal{A}',\mathcal{A}} \;:=\; \langle S^\varepsilon\psi, a_{\varepsilon,2}(q, -i\nabla_q)\,S^\varepsilon\psi\rangle_{L^2(\mathbb{R}^2)}$$

is called *two-scale Wigner functional* $W_2^\varepsilon(\psi) \in \mathcal{A}'$ of the wave function ψ.

We note, that by identity (44) the duality pairing between $W_2^\varepsilon(\psi)$ and a can also be expressed as

$$\langle W_2^\varepsilon(\psi), a\rangle_{\mathcal{A}',\mathcal{A}} \;=\; \int_{\mathbb{R}^4} \mathrm{tr}\left(W^\varepsilon(\psi)(q,p)\, a(q, p, \tfrac{g(q,p)}{\sqrt{\varepsilon}})\right) dq\,dp\,.$$

Therefore, since $W^\varepsilon(\psi) \in C_0(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$, the two-scale Wigner functional $W_2^\varepsilon(\psi)$ can be viewed as the distribution

$$W^\varepsilon(\psi)(q,p)\,\delta(\eta - \tfrac{g(q,p)}{\sqrt{\varepsilon}})\,.$$

The above representation of the two-scale functional $W_2^\varepsilon(\psi)$ also illustrates its dependance on the function g chosen to parameterize the distance to the submanifold I_g. In general, the two-scale functional $W_2^\varepsilon(\psi)$ inherits from the Wigner function $W^\varepsilon(\psi)$ the non-positivity. However, when passing to the semi-classical limit $\varepsilon \to 0$, we expect positivity of the limit points. Indeed, if we additionally assume that there is $m \in \mathbb{N}$ such that

$$\forall (q,p) \in \mathbb{R}^{2n}:\quad |\,\nabla g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)\,| \le \text{ const. } \sqrt{\varepsilon}\;\langle (q,p)\rangle^m\;, \tag{45}$$

then the following two-scale version of the sharp Gårding inequality guarantees positivity when passing to the limit.

Proposition 5 *If the polynomially bounded function* $g \in C^\infty(\mathbb{R}^4, \mathbb{R})$ *satisfies the additional condition (45), then for each non-negative* $0 \le a \in \mathcal{A}$ *there is a positive constant* $C = C(a) > 0$ *such that for all* $\varepsilon > 0$ *and all* $\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)$

$$\langle \psi, a_\varepsilon(q, -i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^2)} \;\ge\; -C\sqrt{\varepsilon}\,\|\psi\|^2_{L^2(\mathbb{R}^2)}\,.$$

The proof follows the steps outlined in Exercise 2.22 of [Ma], which deals with the sharp Gårding inequality for one-scale scalar-valued symbols.

Proof. For $a \in \mathcal{A}$ one defines the anti-Wick symbol

$$a_{\varepsilon,AW}(q,p) \;:=\; \pi^{-2}\int_{\mathbb{R}^4} a_{\varepsilon,2}(q',p')\, e^{-|q-q'|^2-|p-p'|^2}\, dq'\, dp' \;\in\; S^0_0(1)\,.$$

Taylor expansion of $a_{\varepsilon,2}(q',p')$ around the point (q,p) yields

$$a_{\varepsilon,2}(q',p') \;=\; a_{\varepsilon,2}(q,p) \;+\; (q'-q, p'-p)\cdot \int_0^1 (\nabla a_{\varepsilon,2})((1-t)q+tq', (1-t)p+tp')\, dt\,,$$

and since $\int_{\mathbb{R}^4} e^{-|q-q'|^2-|p-p'|^2}\, dq'\, dp' = \pi^2$,

$$\begin{aligned} a_{\varepsilon,AW}(q,p) \;&=\; a_{\varepsilon,2}(q,p) \;+\; \int_{\mathbb{R}^4}\int_0^1 (q'-q, p'-p)\cdot \ldots \\ &\quad \ldots\cdot (\nabla a_{\varepsilon,2})((1-t)q+tq', (1-t)p+tp')\, e^{-|q-q'|^2-|p-p'|^2}\, dt\, dq'\, dp'\,. \end{aligned}$$

Clearly,

$$\begin{aligned} \nabla_q a_{\varepsilon,2}(q,p) \;&=\; \sqrt{\varepsilon}\,(\nabla_q a)(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p, g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)/\sqrt{\varepsilon}) \\ &\quad+\; (\partial_\eta a)(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p, g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)/\sqrt{\varepsilon})\; \nabla_q g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)\,. \end{aligned}$$

Since $|\nabla_q g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)| \le \text{const.}\sqrt{\varepsilon}\,\langle (q,p)\rangle^m$ for some $m \in \mathbb{N}$, and since $\partial_\eta a$ is capable of compensating polynomial growth, we have

$$\nabla_q a_{\varepsilon,2} \;=\; \mathcal{O}(\sqrt{\varepsilon}) \quad \text{in } S^0_0(1)\,.$$

Analogously, $\nabla_p a_{\varepsilon,2} = \mathcal{O}(\sqrt{\varepsilon})$ in $S^0_0(1)$. Therefore, we obtain $c_4(a_{\varepsilon,2} - a_{\varepsilon,AW}) = \mathcal{O}(\sqrt{\varepsilon})$ and

$$\|a_{\varepsilon,2}(q, -i\nabla_q) - a_{\varepsilon,AW}(q, -i\nabla_q)\|_{\mathcal{L}(L^2)} \;=\; \mathcal{O}(\sqrt{\varepsilon})\,. \tag{46}$$

For $\phi \in \mathcal{S}(\mathbb{R}^2, \mathbb{C}^2)$ we have

$$\begin{aligned} a_{\varepsilon,AW}(q, -i\nabla_q)\phi(q) \;&=\; (2\pi)^{-2}\int_{\mathbb{R}^4} e^{i(q-q')\cdot p}\, a_{\varepsilon,AW}(\tfrac{q+q'}{2}, p)\, \phi(q')\, dq'\, dp \\ &=\; (2\pi)^{-2}\,\pi^{-2}\int_{\mathbb{R}^8} e^{i(q-q')\cdot p}\, e^{-|(q+q')/2-x|^2-|p-\xi|^2}\, a_{\varepsilon,2}(x,\xi)\, \phi(q')\, dx\, d\xi\, dq'\, dp\,. \end{aligned}$$

Moreover,

$$\begin{aligned} &\int_{\mathbb{R}^2} e^{i(q-q')\cdot p}\, e^{-|(q+q')/2-x|^2-|p-\xi|^2}\, dp \\ &\quad=\; e^{i(q-q')\cdot\xi}\, e^{-|(q+q')/2-x|^2}\int_{\mathbb{R}^2} e^{i(q-q')\cdot p}\, e^{-|p|^2}\, dp \\ &\quad=\; \pi e^{i(q-q')\cdot\xi}\, e^{-|(q+q')/2-x|^2}\, e^{-|q-q'|^2/4} \;=\; \pi e^{i(q-q')\cdot\xi}\, e^{-|q-x|^2/2-|q'-x|^2/2}\,, \end{aligned}$$

and therefore

$$
\begin{aligned}
&\langle \phi, a_{\varepsilon,AW}(q,-i\nabla_q)\phi\rangle_{L^2(\mathbb{R}^2)} \; = \\
&\quad (2\pi)^{-2}\,\pi^{-1}\int_{\mathbb{R}^8} e^{i(q-q')\cdot\xi}\, e^{-|q-x|^2/2-|q'-x|^2/2}\,\phi(q)\cdot a_{\varepsilon,2}(x,\xi)\,\phi(q')\,dx\,d\xi\,dq'\,dq \; = \\
&\quad (2\pi)^{-2}\,\pi^{-1}\int_{\mathbb{R}^4} \Phi(x,\xi)\cdot a_{\varepsilon,2}(x,\xi)\,\Phi(x,\xi)\,dx\,d\xi \;\geq\; 0
\end{aligned}
$$

with

$$
\Phi(x,\xi) \;:=\; \int_{\mathbb{R}^2} e^{i\,q\cdot\xi}\, e^{-|q-x|^2/2}\,\phi(q)\,dq\,.
$$

By Lemma 10 and equation (46), we have for $\psi \in \mathcal{S}(\mathbb{R}^2,\mathbb{C}^2)$

$$
\begin{aligned}
\langle \psi, a_\varepsilon(q,-i\varepsilon\nabla_q)\psi\rangle_{L^2(\mathbb{R}^n)} &= \langle S^\varepsilon\psi, a_{\varepsilon,2}(q,-i\nabla_q)\,S^\varepsilon\psi\rangle_{L^2(\mathbb{R}^2)} \\
&= \langle S^\varepsilon\psi, a_{\varepsilon,AW}(q,-i\nabla_q)\,S^\varepsilon\psi\rangle_{L^2(\mathbb{R}^2)} \;+\; \mathcal{O}(\sqrt{\varepsilon})\,\|\psi\|^2_{L^2(\mathbb{R}^2)} \\
&\geq\; -\,\mathrm{const.}\,\sqrt{\varepsilon}\,\|\psi\|^2_{L^2(\mathbb{R}^2)}\,.
\end{aligned}
$$

By density, we conclude the proof also for general wave functions $\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)$. □

12.2 Two-Scale Wigner Measures

The Calderón-Vaillancourt Theorem and the previous version of Gårding's inequality are all we need to study the semi-classical limit of two-scale Wigner functionals $W_2^\varepsilon(\psi^\varepsilon)$ for bounded sequences $(\psi^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^2,\mathbb{C}^2)$.

Proposition 6 (Two-Scale Wigner Measures) *Let $(\psi^\varepsilon)_{\varepsilon>0}$ be a bounded sequence in $L^2(\mathbb{R}^2,\mathbb{C}^2)$.*

1. *$(W_2^\varepsilon(\psi^\varepsilon))_{\varepsilon>0}$ has weak*-limit points ρ in $\mathcal{A}'$. All such limit points ρ are bounded positive matrix-valued Radon measures on $\mathbb{R}^4\times\overline{\mathbb{R}}$.*

2. *Let $(W_2^\varepsilon(\psi^\varepsilon))_{\varepsilon>0}$ converge to ρ with respect to the weak*-topology on $\mathcal{A}'$. Then, $(W^\varepsilon(\psi^\varepsilon))_{\varepsilon>0}$ converges to a Wigner measure μ in $\mathcal{S}'(\mathbb{R}^4,\mathcal{L}(\mathbb{C}^2))$, and there exists a bounded positive matrix-valued Radon measure ν on $I_g\times\overline{\mathbb{R}}$, such that*

$$
\begin{aligned}
&\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} a(q,p,\eta)\rho(dp,dq,d\eta) = \\
&\qquad \int_{\mathbb{R}^4\setminus I_g} a(q,p,\infty)\mu(dq,dp) + \int_{I_g\times\overline{\mathbb{R}}} a(q,p,\eta)\nu(dq,dp,d\eta)
\end{aligned}
$$

for all $a \in C_c(\mathbb{R}^4\times\overline{\mathbb{R}},\mathcal{L}(\mathbb{C}^2))$, and we have $\int_{\overline{\mathbb{R}}}\nu(\cdot,d\eta) = \mu|_{I_g}$.

Definition 11 (Two-Scale Wigner Measure) The measures ρ introduced in Proposition 6 are called *two-scale Wigner measures* of the bounded sequence $(\psi^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^2,\mathbb{C}^2)$ with respect to the submanifold $I_g = \{(q,p)\in\mathbb{R}^4 \mid g(q,p)=0\}$.

The previous Proposition 6 is the analogue of Theorem 1 in [FeGe1]. There, admissible observables are required to be constant with respect to η for large η. That property, however, prevents the definition of a semigroup comparable to $\mathcal{L}_\varepsilon^t$ acting on two-scale observables. Thus, we now give a self-contained proof for the construction with observables in $\mathcal{A}$, which is analogous to the construction of Wigner measures presented in Part B, Section 7. In contrast to the proof of C. Fermanian and P. Gérard in [FeGe1], it avoids Fourier integral operators and is just based on the Calderón-Vaillancourt Theorem (Theorem 5) and the two-scale version of the semi-classical sharp Gårding inequality (Proposition 5).

Proof. We proceed via different steps, firstly showing a uniform bound, secondly positivity of the limit points, then extending the linear form to continuous functions, and finally proving the claimed relation to the Wigner measure μ.

A uniform bound. Since $c_4(a_{\varepsilon,2}) \leq s_5(a)$ uniformly in $\varepsilon > 0$, the Calderón-Vaillancourt Theorem gives a positive constant $C > 0$ such that

$$| \langle W_2^\varepsilon(\psi^\varepsilon), a \rangle_{\mathcal{A}',\mathcal{A}} | \leq \; C\, s_5(a)\, \|\psi^\varepsilon\|^2_{L^2(\mathbb{R}^2)}\,.$$

Since $\mathcal{A}$ is a separable topological vector space, an application of the Banach-Alaoglu Theorem, Theorem 3.17 in [Ru], gives a subsequence $(W_2^{\varepsilon_k}(\psi^{\varepsilon_k}))_{\varepsilon_k>0}$, which converges with respect to the weak*-topology to some $\rho \in \mathcal{A}'$.

Positivity. By Proposition 5, we have for non-negative $0 \leq a \in \mathcal{A}$

$$\begin{aligned}\langle \rho, a \rangle_{\mathcal{A}',\mathcal{A}} \;&=\; \lim_{k\to\infty} \langle W_2^{\varepsilon_k}(\psi^{\varepsilon_k}), a \rangle_{\mathcal{A}',\mathcal{A}} \;=\; \lim_{k\to\infty} \langle \psi^{\varepsilon_k}, a_\varepsilon(q, -i\varepsilon_k \nabla_q)\psi^{\varepsilon_k} \rangle_{L^2(\mathbb{R}^2)}\\ &\geq\; -\mathrm{const.} \lim_{k\to\infty} \sqrt{\varepsilon_k}\, \|\psi^{\varepsilon_k}\|^2_{L^2(\mathbb{R}^2)} \;=\; 0\,.\end{aligned}$$

Thus, ρ is a as bounded positive linear form on $\mathcal{A}$.

Extension to $C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$. The following considerations coincide literally with the standard arguments showing that positive distributions are Radon measures. However, since we have to work with matrix-valued measures on $\mathbb{R}^4 \times \overline{\mathbb{R}}$, we follow up the usual argumentation ensuring that the matrix-valuedness and the set $\{\eta = \infty\}$ do not enforce any alterations. For $a \in \mathcal{A}$ with values in $\mathcal{L}_{sa}(\mathbb{C}^2)$ we have $\|a\|_\infty \pm a \geq 0$, where $\|a\|_\infty = \sup_{(q,p,\eta)\in\mathbb{R}^5} \|a(q,p,\eta)\|_{\mathcal{L}(\mathbb{C}^2)}$. Therefore, $\|a\|_\infty\, \rho(\mathrm{Id}) \pm \rho(a) \geq 0$, that is

$$|\rho(a)| \;\leq\; \rho(\mathrm{Id})\, \|a\|_\infty\,.$$

For arbitrary $a \in \mathcal{A}$, we choose $\theta \in \mathbb{R}$ such that $e^{i\theta}\rho(a) \in \mathbb{R}$. Since $\rho(a^*) = \overline{\rho(a)}$, we have by the preceding observation

$$|\rho(a)| \;=\; \tfrac{1}{2}\, |\rho(e^{i\theta} a + e^{-i\theta} a^*)| \;\leq\; \rho(\mathrm{Id})\, \tfrac{1}{2}\, \|e^{i\theta} a + e^{-i\theta} a^*\|_\infty \;\leq\; \rho(\mathrm{Id})\, \|a\|_\infty\,. \tag{47}$$

Clearly, we can identify $C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$ with the space

$$\begin{aligned}\{\, a \in C(\mathbb{R}^5, \mathcal{L}(\mathbb{C}^2)) : \quad & \mathrm{supp}(a) \subset K \times \mathbb{R} \text{ for some compact set } K \subset \mathbb{R}^4\,,\\ & \exists\, a_\infty \in C(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2)) : \lim_{|\eta|\to\infty} \|a(\cdot,\eta) - a_\infty\|_\infty = 0\,\}\,,\end{aligned}$$

and thus we can view $\mathcal{A}$ as a subspace of $C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$. For $\delta > 0$ and $\phi_\delta \in \mathcal{A}$ with $\int_{\mathbb{R}^5} \phi_\delta(x)\,dx = 1$ and $\mathrm{supp}(\phi_\delta) \subset \{x \in \mathbb{R}^5 : |x| \leq \delta\}$ one immediately checks that the convolution $a * \phi_\delta$ is a function in $\mathcal{A}$, and that $\mathcal{A}$ is dense in $C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$ with respect to the supremum norm. By the bound obtained in (47), ρ extends uniquely to a bounded positive linear form on $C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$. By the Riesz representation Theorem, ρ is a bounded positive Radon measure on $\mathbb{R}^4 \times \overline{\mathbb{R}}$.

Relation to the Wigner measure. Let $(W_2^\varepsilon(\psi^\varepsilon))_{\varepsilon>0}$ converge to $\rho \in \mathcal{A}'$. Since any test function $a \in \mathcal{S}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$ can be viewed as an η-independent observable in $\mathcal{A}$, we have for such functions a

$$\lim_{\varepsilon\to 0} \langle W^\varepsilon(\psi^\varepsilon), a\rangle_{\mathcal{S}',\mathcal{S}} = \lim_{\varepsilon\to 0} \langle W_2^\varepsilon(\psi^\varepsilon), a\rangle_{\mathcal{A}',\mathcal{A}} .$$

Thus, $(\langle W^\varepsilon(\psi^\varepsilon), a\rangle_{\mathcal{S}',\mathcal{S}})_{\varepsilon>0}$ converges for all $a \in \mathcal{S}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$. For $a \in \mathcal{A}_{I_g}$ with

$$\mathcal{A}_{I_g} := \{\, a \in \mathcal{A} \mid \mathrm{supp}(a) \cap (I_g \times \mathbb{R}) = \emptyset\,,\ \lim_{|\eta|\to\infty} c_4(a(\cdot,\eta) - a_\infty) = 0\}$$

there exists $c = c(a) > 0$ such that $|g(q,p)| \geq c$ for all (q,p) in the support of a, and hence $|g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)/\sqrt{\varepsilon}| \geq c/\sqrt{\varepsilon}$ for all $(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)$ in the support of a. We obtain for all $\alpha \in \mathbb{N}_0^4$ with $|\alpha| \leq 5$

$$\begin{aligned}\lim_{\varepsilon\to 0} \sup_{(q,p)\in\mathbb{R}^4} &| \,\partial^\alpha a(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p, g(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)/\sqrt{\varepsilon}) - \partial^\alpha a_\infty(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)\,| \\ &\leq \lim_{|\eta|\to\infty} c_4(a(\cdot,\eta) - a_\infty) = 0 .\end{aligned}$$

Denoting $(q,p) \mapsto a_{\infty,\varepsilon}(q,p) := a_\infty(\sqrt{\varepsilon}q, \sqrt{\varepsilon}p)$, we have $\lim_{\varepsilon\to 0} c_4(a_{\varepsilon,2} - a_{\infty,\varepsilon}) = 0$ and therefore by the Calderón-Vaillancourt Theorem

$$\begin{aligned}\langle \rho, a\rangle_{\mathcal{A}',\mathcal{A}} &= \lim_{\varepsilon\to 0} \langle S^\varepsilon\psi^\varepsilon, a_{\varepsilon,2}(q, -i\nabla_q)\, S^\varepsilon\psi^\varepsilon\rangle_{L^2} = \lim_{\varepsilon\to 0} \langle S^\varepsilon\psi^\varepsilon, a_{\infty,\varepsilon}(q, -i\nabla_q)\, S^\varepsilon\psi^\varepsilon\rangle_{L^2} \\ &= \lim_{\varepsilon\to 0} \langle \psi^\varepsilon, a_\infty(q, -i\varepsilon\nabla_q)\, \psi^\varepsilon\rangle_{L^2} = \int_{\mathbb{R}^4} \mathrm{tr}\,(a_\infty(q,p)\, \mu(dq,dp)) .\end{aligned}$$

By the same arguments employed before, we can approximate $a \in C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$ with support away from I_g by observables in $(a * \phi_\delta)_{\delta>0}$ in $\mathcal{A}_{I_g}$ with support away from I_g, since $|g(q,p)| \geq c$ for (q,p) in the support of a implies $|g(q',p')| \geq c'$ for some $c' = c'(\delta) > 0$ for all (q',p') in the support of $a * \phi_\delta$, and since for all $\alpha \in \mathbb{N}_0^4$ with $|\alpha| \leq 5$

$$\lim_{|\eta|\to\infty} \|\partial^\alpha\,((a * \phi_\delta)(\cdot,\eta) - a_\infty * \phi_{\delta,\infty})\,\|_\infty \leq \lim_{|\eta|\to\infty} \|\partial^\alpha\,(a(\cdot,\eta) - a_\infty)\,\|_\infty\, \|\phi_\delta\|_{L^1(\mathbb{R}^5)} = 0 .$$

Thus,

$$\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\,(a(q,p,\eta)\, \rho(dq,dp,d\eta)) = \int_{\mathbb{R}^4} \mathrm{tr}\,(a(q,p,\infty)\, \mu(dq,dp)) .$$

Inserting $a \in \mathcal{S}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$ of the form

$$\begin{pmatrix} \tilde{a} & 0 \\ 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & \tilde{a} \\ 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & 0 \\ \tilde{a} & 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} 0 & 0 \\ 0 & \tilde{a} \end{pmatrix},$$

with $\widetilde{a} \in \mathcal{S}(\mathbb{R}^4, \mathbb{C})$, we can remove the traces and obtain for all $a \in C_c(\mathbb{R}^4 \times \overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$ with $\mathrm{supp}(a) \cap (I_g \times \overline{\mathbb{R}}) = \emptyset$

$$\int_{\mathbb{R}^4 \times \overline{\mathbb{R}}} a(q,p,\eta)\, \rho(dq,dp,d\eta) \;=\; \int_{\mathbb{R}^4} a(q,p,\infty)\, \mu(dq,dp)\,,$$

which means

$$\rho|_{(\mathbb{R}^4 \setminus I_g)\times\overline{\mathbb{R}}}(q,p,\eta) \;=\; \mu|_{\mathbb{R}^4\setminus I_g}(q,p) \otimes \delta(\eta-\infty)\,, \qquad (q,p,\eta) \in \mathbb{R}^4 \times \overline{\mathbb{R}}\,.$$

Defining $\nu := \rho|_{I_g \times \overline{\mathbb{R}}}$ as the restriction of the measure ρ to $I_g \times \overline{\mathbb{R}}$, we obtain

$$\rho(q,p,\eta) \;=\; \mu|_{\mathbb{R}^4\setminus I_g}(q,p) \otimes \delta(\eta-\infty) \;+\; \nu(q,p,\eta)\,.$$

For $a(q,p) = a \in \mathcal{A}$ just depending on (q,p) we have

$$\int_{\mathbb{R}^4 \times \overline{\mathbb{R}}} \mathrm{tr}\left(a(q,p)\, \rho(dq,dp,d\eta)\right) = \lim_{\varepsilon\to 0} \langle \psi^\varepsilon, a(q,-i\varepsilon\nabla_q)\psi^\varepsilon\rangle_{L^2} = \int_{\mathbb{R}^4} \mathrm{tr}\left(a(q,p)\, \mu(dq,dp)\right)\,,$$

and thus $\int_{\overline{\mathbb{R}}} \nu(\cdot, d\eta) = \mu|_{I_g}$. □

As the two-scale Wigner functional $W_2^\varepsilon(\psi)$, the measures ρ and ν depend on the function $g(q,p)$ chosen to describe the submanifold I_g. If $\widetilde{g} \in C^\infty(\mathbb{R}^4, \mathbb{R})$ is another function with $I_g = \{(q,p) \in \mathbb{R}^4 \mid \widetilde{g}(q,p) = 0\}$ sharing the same growth properties as g, then for $a \in \mathcal{A}$ the scaled function

$$\widetilde{a}_\varepsilon(q,p) \;:=\; a(q,p,\tfrac{\widetilde{g}(q,p)}{\sqrt{\varepsilon}})$$

is in $C_b^\infty(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$. Moreover, there exists $f \in C^\infty(\mathbb{R}^4, \mathbb{R})$ with $f(q,p) \neq 0$ for all (q,p) such that $\widetilde{g}(q,p) = f(q,p)g(q,p)$, and setting $a_f(q,p,\eta) := a(q,p,f(q,p)\eta)$ we clearly have $\widetilde{a}_\varepsilon = (a_f)_\varepsilon$. Thus, repeating the corresponding two-scale construction and denoting the resulting measures by $\widetilde{\rho}$ and $\widetilde{\nu}$, we obtain

$$\rho(q,p,f^{-1}(q,p)\eta) \;=\; \widetilde{\rho}(q,p,\eta)\,, \qquad \nu(q,p,f^{-1}(q,p)\eta) \;=\; \widetilde{\nu}(q,p,\eta)\,. \tag{48}$$

In the following, we discuss three examples for two-scale Wigner measures associated with the submanifold $I = \{(q,p) \in \mathbb{R}^4 \mid q \wedge p = 0\}$, which is relevant for the dynamics of the model problem (1). For simplicity, the considered functions are all scalar-valued. The employed Fourier transform $\widehat{u}(p) = \int e^{-iq\cdot p}\, u(q)\, dq$ is is neither normalized nor scaled in the semi-classical parameter ε.

Coherent States. We start with some coherent states of the form

$$\psi^\varepsilon(q) \;=\; \varepsilon^{-\beta}\, \Phi\big(\varepsilon^{-\beta}(q - q_0 - \varepsilon^\gamma \eta_0)\big)\, e^{i p_0 \cdot q/\varepsilon}$$

with $\Phi \in L^2(\mathbb{R}^2, \mathbb{C})$, $\beta \in]0,1]$, $0 < \gamma < \beta$, and $q_0, p_0, \eta_0 \in \mathbb{R}^2$ with $q_0 \wedge p_0 = 0$. If we choose $\beta = \frac{1}{2}$, $\eta_0 = 0$, and $\Phi(q) = \pi^{-1/2}(\det A)^{-1} \exp\big((q \cdot BA^{-1}q)/2\big)$ with matrices $A, B \in GL(2, \mathbb{C})$ satisfying condition (17), then ψ^ε is the zeroth semi-classical wave packet ϕ_0

as defined before in (16). We have for scalar-valued test functions $a \in \mathcal{A}$

$$\int_{R^4} W^\varepsilon(\psi^\varepsilon)(q,p)\, a\big(q,p,\tfrac{q\wedge p}{\sqrt{\varepsilon}}\big)\, dq\, dp \;=$$

$$(2\pi)^{-2}\int_{\mathbb{R}^6} e^{i y\cdot p}\, \Phi(q-y/2)\,\overline{\Phi}(q+y/2)\ldots$$

$$\ldots a\big(q_0+\varepsilon^\beta q+\varepsilon^\gamma \eta_0\,,p_0+\varepsilon^{1-\beta}p\,,\varepsilon^{-1/2}\,d(q,p)\big)\, dy\, dq\, dp\,,$$

where $d(q,p) = \varepsilon\, q\wedge p + \varepsilon^\beta\, q\wedge p_0 + \varepsilon^{1-\beta}\, q_0\wedge p + \varepsilon^{1+\gamma-\beta}\,\eta_0\wedge p + \varepsilon^\gamma\,\eta_0\wedge p_0$, so that

$$\varepsilon^{-1/2}\, d(q,p) \;=\; \varepsilon^{\beta-\frac{1}{2}}\, q\wedge p_0 + \varepsilon^{\frac{1}{2}-\beta}\, q_0\wedge p + \varepsilon^{\gamma-\frac{1}{2}}\,\eta_0\wedge p_0 + o(\varepsilon^{\frac{1}{2}-\beta}) + o(1)\,. \qquad (49)$$

Ignoring the η-component of $a(q,p,\eta)$, we obtain the Wigner measure of $(\psi^\varepsilon)_{\varepsilon>0}$

$$\mu(q,p) \;=\; \|\Phi\|^2_{L^2}\; \delta_{(q_0,p_0)}(q,p)\,,$$

which shows, that $(\psi^\varepsilon)_{\varepsilon>0}$ concentrates on $I = \{q\wedge p = 0\}$. However, the two-scale measure for I with scale $\sqrt{\varepsilon}$ depends on η_0 and γ. If $\beta = \frac{1}{2}$ and $\eta_0\wedge p_0 = 0$, then the concentration of $(\psi^\varepsilon)_{\varepsilon>0}$ on I is issued from finite distance. Otherwise, the concentration occurs from infinite distance (versus $\sqrt{\varepsilon}$). Below, we discuss some significant cases. For simplicity, we assume $|q_0| = |p_0| = 1$.

$\beta = \frac{1}{2}$ and $\eta_0\wedge p_0 = 0$: The dominating term in (49) is $q\wedge p_0 + q_0\wedge p$. Setting $\Psi(q) := \exp\big(-\frac{i}{2}|q|^2\,\mathrm{sgn}(q_0\cdot p_0)\big)\,\Phi(q)$, we obtain

$$\rho(q,p,\eta) \;=\; \delta_{(q_0,p_0)}(q,p)\otimes(2\pi)^{-2}\left(\int_{\mathbb{R}} |\,\widehat{\Psi}(tq_0+\eta q_0^\perp)\,|^2\, dt\right) d\eta\,.$$

$\gamma < \beta = \frac{1}{2}$ and $\eta_0\wedge p_0 \neq 0$: The dominating term in (49) is $\varepsilon^{\gamma-1/2}\,\eta_0\wedge p_0$, and we get

$$\rho(q,p,\eta) \;=\; \mu(q,p)\otimes\delta_\infty(\eta)\,.$$

$\gamma < \beta < \frac{1}{2}$: The dominating term in (49) is $\varepsilon^{\gamma-1/2}\,\eta_0\wedge p_0$ if $\eta_0\wedge p_0 \neq 0$ and $\varepsilon^{\beta-1/2}\, q\wedge p_0$ if $\eta_0\wedge p_0 = 0$. In both cases, we obtain as before

$$\rho(q,p,\eta) \;=\; \mu(q,p)\otimes\delta_\infty(\eta)\,.$$

The case $\beta > \frac{1}{2}$ leads to a similar discussion with results depending on the sign of $\gamma-(1-\beta)$.

Arbitrary Phase. Replacing the linear phase by an arbitrary one, we now consider families of the form

$$\psi^\varepsilon(q) \;=\; \varepsilon^{-\beta}\;\Phi\big(\varepsilon^{-\beta}(q-q_0)\big)\;\exp\big(\tfrac{i}{2\varepsilon}\,f(|q|^2)\big)$$

with $\Phi \in L^2(\mathbb{R}^2,\mathbb{C})$, $f \in C^1(\mathbb{R},\mathbb{R})$, $0<\beta<1$, and $q_0 \in \mathbb{R}^2\setminus\{0\}$. Writing

$$\begin{aligned} & f(\,|\,q_0+\varepsilon^\beta\, z\,|^2\,) - f(\,|\,q_0+\varepsilon^\beta\, z'\,|^2\,) \\ &\quad =\; 2\varepsilon^\beta\,(z-z')\cdot\big(q_0+\varepsilon^\beta\,\tfrac{z+z'}{2}\big)\int_0^1 f'\big(t\,|q_0+\varepsilon^\beta z|^2+(1-t)\,|q_0+\varepsilon^\beta z'|^2\big)\,dt \\ &\quad =:\; 2\,\varepsilon^\beta\,(z-z')\cdot\big(q_0+\varepsilon^\beta\,\tfrac{z+z'}{2}\big)\; l^\varepsilon(q_0,z,z') \end{aligned}$$

for $z, z' \in \mathbb{R}^2$, we calculate for scalar-valued $a \in \mathcal{A}$

$$\int_{\mathbb{R}^4} W^\varepsilon(\psi^\varepsilon)(q,p)\, a\big(q,p,\tfrac{q\wedge p}{\sqrt{\varepsilon}}\big)\, dq\, dp \;=$$

$$(2\pi)^{-2}\int_{\mathbb{R}^6} e^{i\,y\cdot p}\,\Phi(q-y/2)\,\overline{\Phi}(q+y/2)\dots$$

$$\dots a\big(q_0+\varepsilon^\beta q, l^\varepsilon(q_0, q+y/2, q-y/2)(q_0+\varepsilon^\beta q)+\varepsilon^{1-\beta}\,p, \varepsilon^{-1/2}\, d(q,p)\big)\, dy\, dq\, dp\,,$$

with

$$\varepsilon^{-1/2}\, d(q,p) \;=\; \varepsilon^{\frac12-\beta}\,(q_0+\varepsilon^\beta q)\wedge p \;=\; \varepsilon^{\frac12-\beta}\, q_0\wedge p + o(1)\,.$$

Since $\lim_{\varepsilon\to 0} l^\varepsilon(q_0,z,z') = f'(|q_0|^2)$, we obtain the Wigner measure

$$\mu(q,p) \;=\; \|\Phi\|^2_{L^2}\;\delta_{(0,0)}\big(q-q_0, p-f'(|q_0|)^2\,q_0\big)\,,$$

and have again concentration on $I=\{q\wedge p = 0\}$. However, $\sqrt{\varepsilon}$-concentration is issued from finite distance if and only if $\beta\le\frac12$. We distinguish three different cases, assuming that $|q_0|=1$.

$$\beta<\tfrac12: \qquad \rho(q,p,\eta) = \mu(q,p)\otimes\delta_0(\eta)\,,$$

$$\beta=\tfrac12: \qquad \rho(q,p,\eta) = \delta_{(q_0,f'(1)q_0)}(q,p)\otimes(2\pi)^{-2}\Big(\int_{\mathbb{R}} |\,\widehat{\Phi}(tq_0+\eta q_0^\perp)\,|^2\, dt\Big)\, d\eta\,,$$

$$\beta>\tfrac12: \qquad \rho(q,p,\eta) = \mu(q,p)\otimes\delta_\infty(\eta)\,.$$

Concentration on a Circle. Finally, we consider families of the form

$$\psi^\varepsilon(q) \;=\; \varepsilon^{-\frac14}\;\Phi\Big(\tfrac{|q|^2-R^2}{\sqrt{\varepsilon}}\Big)\;\exp\big(\tfrac{i}{2\varepsilon}\,|q-\varepsilon^\gamma q_0|^2\big),$$

where $\Phi\in C_c^\infty(\mathbb{R},\mathbb{C})$, $q_0\in\mathbb{R}^2$, $R\in\,]0,\infty[$, and $\gamma\in\,]0,1[$. Since we will apply the stationary phase method in the following, we work with scalar-valued $a\in\mathcal{A}$, which are compactly supported in (q,p). We have

$$I^\varepsilon \;:=\; \int_{\mathbb{R}^4} W^\varepsilon(\psi^\varepsilon)(q,p)\, a\big(q,p,\tfrac{q\wedge p}{\sqrt{\varepsilon}}\big)\, dq\, dp \;=$$

$$(2\pi)^{-2}\,\varepsilon^{-1/2}\int_{\mathbb{R}^6} e^{i\,y\cdot p}\;\Phi\Big(\tfrac{|q-y/2|^2-R^2}{\sqrt{\varepsilon}}\Big)\;\overline{\Phi}\Big(\tfrac{|q+y/2|^2-R^2}{\sqrt{\varepsilon}}\Big)\dots$$

$$\dots a\big(q, q-\varepsilon^\gamma\, q_0+\varepsilon\, p, \sqrt{\varepsilon}\, q\wedge p+\varepsilon^{\gamma-\frac12}\, q_0\wedge q\big)\, dy\, dq\, dp\,,$$

and thus by the Fourier inversion formula

$$I^\varepsilon \;=\; (2\pi)^{-4}\,\varepsilon^{-1/2}\int_{\mathbb{R}^8} a(q, q-\varepsilon^\gamma\, q_0+\varepsilon p, \sqrt{\varepsilon}\, q\wedge p+\varepsilon^{\gamma-1/2}\, q_0\wedge p)\,\widehat{\Phi}(\mu-\nu/2)\dots$$

$$\dots\overline{\widehat{\Phi}}(\mu+\nu/2)\, e^{i\,y\cdot p}\, e^{-2\,i\,\mu\, q\cdot y/\sqrt{\varepsilon}}\;\exp\big(-i\nu\,\big(|q|^2+|y|^2/4-R^2\big)/\sqrt{\varepsilon}\big)\, d\mu\, d\nu\, dy\, dq\, dp\,.$$

Substituting $p = 2\,\varepsilon^{-1/2}\,\mu q+\varepsilon^{-1/4}\,\zeta$ and $y=\varepsilon^{1/4}\, z$, we obtain

$$I^\varepsilon \;=\; (2\pi)^{-4}\,\varepsilon^{-\frac12}\int_{\mathbb{R}^8} a\big(q, q-\varepsilon^\gamma\, q_0+2\sqrt{\varepsilon}\,\mu\, q+\varepsilon^{\frac34}\,\zeta, \varepsilon^{\frac14}\, q\wedge\zeta+\varepsilon^{\gamma-\frac12}\, q_0\wedge q\big)\dots$$

$$\dots\;\widehat{\Phi}(\mu-\nu/2)\,\overline{\widehat{\Phi}}(\mu+\nu/2)\;\exp(iz\cdot\zeta-\tfrac{i}{4}\,\nu\,|z|^2)\dots$$

$$\dots\exp\big(-i\nu\,\big(|q|^2-R^2\big)/\sqrt{\varepsilon}\big)\, d\mu\, d\nu\, dz\, dq\, d\zeta\,.$$

We apply the method of stationary phase, see for example Proposition 5.2 in in [DiSj], in the variables $\nu \in \mathbb{R}$ and $r = |q| \in [0, \infty[$ with large parameter $1/\sqrt{\varepsilon}$. The phase function $(\nu, r) \mapsto -\nu(r^2 - R^2)$ has the non-degenerate critical point $(0, R)$, and we obtain for all $u \in C_c^\infty([0, \infty[\times\mathbb{R}, \mathbb{C})$

$$(2\pi)^{-1}\, \varepsilon^{-1/2} \int_{[0,\infty[\times\mathbb{R}} e^{-i\nu(r^2-R^2)}\, u(\nu, \rho)\, r\, dr\, d\nu \;\sim\; u(0, R) \qquad \text{as} \quad \varepsilon \to 0\,.$$

Hence, by Parseval's relation and Fourier inversion formula

$$I^\varepsilon \;\sim\; \|\Phi\|_{L^2}^2 \int_{\{|q|=R\}} a(q, q, \varepsilon^{\gamma-\frac{1}{2}}\, q_0 \wedge q)\, dq \qquad \text{as} \quad \varepsilon \to 0\,.$$

Therefore, the Wigner measure is

$$\mu(q, p) \;=\; \|\Phi\|_{L^2}^2\; \mathbb{1}_{\{|q|=R\}}(q)\, dq \otimes \delta_q(p)\,,$$

and we observe once again concentration on $I = \{q \wedge p = 0\}$. The two-scale measure provides additional information concerning the exponent γ and the direction q_0. There are three different cases.

$$\begin{aligned}
\gamma < \tfrac{1}{2}: &\qquad \rho(q,p,\eta) = \mu(q,p) \otimes \delta_\infty(\eta)\,,\\
\gamma = \tfrac{1}{2}: &\qquad \rho(q,p,\eta) = \mu(q,p) \otimes \delta_{q_0\wedge q}(\eta)\,,\\
\gamma > \tfrac{1}{2}: &\qquad \rho(q,p,\eta) = \mu(q,p) \otimes \delta_0(\eta)\,.
\end{aligned}$$

12.3 Propagation of Two-Scale Wigner Functionals

Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ be the solution of the Schrödinger equation (1) with initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ and $g(q,p) = q \wedge p$. The two-scale Wigner functional inherits the solution's continuous time dependence, that is

$$W_2^\varepsilon(\psi^\varepsilon(t)) \in C(\mathbb{R}, \mathcal{A}')\,,$$

where continuity is understood with respect to the strong dual topology on $\mathcal{A}'$. Indeed, for bounded subsets $B \subset \mathcal{A}$, that is $\sup_{a\in B} \|\langle(q,p)\rangle^\beta \partial^\gamma a\|_\infty < \infty$ for all $\beta \in \mathbb{N}_0$ and $\gamma \in \mathbb{N}_0^5$, we have for $t, t' \in \mathbb{R}$

$$\begin{aligned}
&\sup_{a\in B}\, |\, \langle W_2^\varepsilon(\psi^\varepsilon(t)) - W_2^\varepsilon(\psi^\varepsilon(t')), a\rangle_{\mathcal{A}',\mathcal{A}}\, | \le \\
&\qquad \sup_{a\in B}\, s_5(a)\;\; \|\psi^\varepsilon(t) - \psi^\varepsilon(t')\|_{L^2(\mathbb{R}^2)} \left(\|\psi^\varepsilon(t)\|_{L^2(\mathbb{R}^2)} + \|\psi^\varepsilon(t')\|_{L^2(\mathbb{R}^2)} \right)\,,
\end{aligned}$$

and thus the asserted continuity with respect to time. However, passing to the limit $\varepsilon \to 0$, we are confronted with the possibility that different points of time t could require different subsequences $(\varepsilon_k(t))_{k\in\mathbb{N}}$ for convergence to a two-scale measure. In that case, neither continuity with respect to time nor other properties of the two-scale Wigner functional would carry over to the two-scale measures. In the scalar-valued case, that scenario is ruled out by the Egorov Theorem, see Corollary 3 in Part B. Here, in the matrix-valued case we have to restrict the analysis to diagonal observables.

PROPOSITION 7 *Let* $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2,\mathbb{C}^2))$ *be the solution of the Schrödinger equation (1) with initial data* $(\psi_0^\varepsilon)_{\varepsilon>0}$ *bounded* $L^2(\mathbb{R}^2,\mathbb{C}^2)$ *such that* $(W_2^\varepsilon(\psi_0^\varepsilon))_{\varepsilon>0}$ *converges to a two-scale measure* ρ_0 *in* $\mathcal{A}'$.

1. *Then, for every* $T > 0$ *there is a subsequence* $(\varepsilon_k)_{k\in\mathbb{N}}$ *such that*

$$\lim_{k\to\infty} \langle W_2^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\rangle_{\mathcal{A}',\mathcal{A}} \qquad \text{and} \qquad \lim_{k\to\infty} \langle W^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\rangle_{\mathcal{S}',\mathcal{S}}$$

exist uniformly in $t \in [0,T]$ *for all* $a \in \mathcal{A}$ *and* $a \in \mathcal{S}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$, *respectively, with vanishing commutator* $[a, V] = 0$ *and* $\operatorname{supp}(a) \cap \{q = 0\} = \emptyset$.

2. *For scalar-valued* a *with the same properties, the limits*

$$\lim_{k\to\infty} \left\langle W_2^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\Pi^\pm\right\rangle_{\mathcal{A}',\mathcal{A}} =: \left\langle \rho_t^\pm, a\Pi^\pm\right\rangle_{\mathcal{A}',\mathcal{A}}$$

and

$$\lim_{k\to\infty} \left\langle W^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\Pi^\pm\right\rangle_{\mathcal{S}',\mathcal{S}} =: \left\langle \mu_t^\pm, a\Pi^\pm\right\rangle_{\mathcal{S}',\mathcal{S}}$$

define positive bounded scalar-valued Radon measures $\rho_t^\pm$ *and* $\mu_t^\pm$ *on* $(\mathbb{R}^4 \setminus \{q = 0\}) \times \overline{\mathbb{R}}$ *and* $\mathbb{R}^4 \setminus \{q = 0\}$, *respectively, for all* $t \in [0,T]$.

3. *For scalar-valued observables* a *with the same properties, we have convergence of the full sequence*

$$\lim_{\varepsilon\to 0} \left\langle W_2^\varepsilon(\psi^\varepsilon(t)) - W_2^\varepsilon(\psi_0^\varepsilon) \circ \Phi_\pm^{-t}, a\,\Pi^\pm\right\rangle_{\mathcal{A}',\mathcal{A}} = \lim_{\varepsilon\to 0} \left\langle W^\varepsilon(\psi^\varepsilon(t)) - W^\varepsilon(\psi_0^\varepsilon) \circ \Phi_\pm^{-t}, a\,\Pi^\pm\right\rangle_{\mathcal{S}',\mathcal{S}} = 0$$

uniformly on time intervals $[0,T]$ *such that for all* $t \in [0,T]$

$$\bigcup_{j\in\{\pm\}} \{\Phi_j^t(q,p) \mid \exists \eta \in \overline{\mathbb{R}} : (q,p,\eta) \in \operatorname{supp}(\rho_0)\} \cap \{q = 0\} = \emptyset\,.$$

REMARK 16 Without incorporating non-adiabatic transitions, convergence of the full sequence is only obtained on time-intervals, where the leading order dynamics can be described purely by classical transport. However, the uniform convergence of subsequences on arbitrary time intervals $[0,T]$ will later on be extended to convergence of the full sequence in the proof of Theorem 8. $\diamondsuit$

PROOF. We write $a = \Pi^+ a\Pi^+ + \Pi^- a\Pi^-$ and study

$$\left\langle W_2^\varepsilon(\psi^\varepsilon(t)), \Pi^\pm\, a\,\Pi^\pm\right\rangle_{\mathcal{A}',\mathcal{A}} = \left\langle \psi^\varepsilon(t), (\Pi^\pm\, a_\varepsilon \Pi^\pm)(q, -i\varepsilon\nabla_q)\, \psi^\varepsilon(t)\right\rangle_{L^2(\mathbb{R}^2)}\,.$$

The assertions for the one-scale Wigner transform will follow immediately from the corresponding statements for the two-scale transform.

As the first step, we establish the claimed uniform convergence with respect to time t. Let $\phi \in C_b^\infty(\mathbb{R}^2,\mathbb{R})$ such that $\phi = 1$ on $\{q \in \mathbb{R}^2 \mid \exists(q,\eta) \in \mathbb{R}^3 : (q,p,\eta) \in \operatorname{supp}(a)\}$ and $\phi(0) = 0$. We have by Lemma 5

$$\Pi^\pm a_\varepsilon \Pi^\pm - (\phi^2\Pi^\pm)\,\sharp_\varepsilon\, a_\varepsilon\,\sharp_\varepsilon\,(\phi^2\Pi^\pm) \in S_{1/2}^{-1/2}(1)$$

and therefore

$$\left\langle W_2^\varepsilon(\psi^\varepsilon(t)), \Pi^\pm\, a\, \Pi^\pm \right\rangle_{\mathcal{A}',\mathcal{A}} = \\ \left\langle (\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t), a_\varepsilon(q,-i\varepsilon\nabla_q)(\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t)\right\rangle_{L^2(\mathbb{R}^2)} + \mathcal{O}(\sqrt{\varepsilon})\,.$$

We denote $\lambda_0^\pm(q,p) = \frac{1}{2}|p|^2 \pm |q|$ and choose initial data ψ_0^ε in $D(H^\varepsilon)$. We observe, that the first summand on the right hand side of the previous equation defines a continuously differentiable function $f^\varepsilon_{\psi_0^\varepsilon} : \mathbb{R} \to \mathbb{C}$,

$$t \mapsto f^\varepsilon_{\psi_0^\varepsilon}(t) := \left\langle (\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t), a_\varepsilon(q,-i\varepsilon\nabla_q)(\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t)\right\rangle_{L^2(\mathbb{R}^2)}.$$

We have for the derivative

$$\begin{aligned} \tfrac{d}{dt} f^\varepsilon_{\psi_0^\varepsilon}(t) &= (i\varepsilon)^{-1}\left\langle (\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)H^\varepsilon\psi^\varepsilon(t), (a_\varepsilon)(q,-i\varepsilon\nabla_q)(\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t)\right\rangle \\ &- (i\varepsilon)^{-1}\left\langle (\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t), a_\varepsilon(q,-i\varepsilon\nabla_q)(\phi^2\Pi^\pm)(q,-i\varepsilon\nabla_q)H^\varepsilon\psi^\varepsilon(t)\right\rangle. \end{aligned}$$

We want to show that $\sup_{\varepsilon>0}\|\frac{d}{dt}f^\varepsilon_{\psi_0^\varepsilon}(\cdot)\|_\infty < \infty$ to apply the Arzela-Ascoli Theorem. Since $\nabla(\phi\lambda_0^\pm) \in S_0^0(1)$, semi-classical calculus gives

$$(\phi^2\Pi^\pm)\sharp_\varepsilon h - (\phi\lambda_0^\pm)\sharp_\varepsilon(\phi\Pi^\pm) \in S_0^{-1}(1)\,.$$

Thus, it remains to prove a uniform bound in ε and t for

$$(i\varepsilon)^{-1}\left\langle (\phi\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t), [\phi\lambda_0^\pm, a_\varepsilon]_{\sharp_\varepsilon}(q,-i\varepsilon\nabla_q)(\phi\Pi^\pm)(q,-i\varepsilon\nabla_q)\psi^\varepsilon(t)\right\rangle_{L^2} \tag{50}$$

However, $[\phi\lambda_0^\pm, a_\varepsilon]_{\sharp_\varepsilon} \in S^{-1}_{1/2}(1)$, since $[\phi\lambda_0^\pm, a_\varepsilon] = 0$ and

$$\{\phi\lambda_0^\pm, a_\varepsilon\} = \{\lambda_0^\pm, a_\varepsilon\} = \nabla_p\lambda_0^\pm (D_q a)_\varepsilon - \nabla_q\lambda_0^\pm(D_p a)_\varepsilon\,,$$

where the last identity uses that $\{\lambda_0^\pm, q\wedge p\} = 0$ on $\mathbb{R}^4\setminus\{q=0\}$. Choosing general initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2,\mathbb{C}^2)$ and $\psi \in D(H^\varepsilon)$, we clearly have for $s,t\in\mathbb{R}$

$$|\, f^\varepsilon_{\psi_0^\varepsilon}(s) - f^\varepsilon_{\psi_0^\varepsilon}(t)\,| \le |\, f^\varepsilon_{\psi_0^\varepsilon}(s) - f^\varepsilon_{\psi}(s)\,| + |\, f^\varepsilon_{\psi}(s) - f^\varepsilon_{\psi}(t)\,| + |\, f^\varepsilon_{\psi}(t) - f^\varepsilon_{\psi_0^\varepsilon}(t)\,|\ .$$

Denoting the strongly continuous one-parameter group of H^ε by $(U^\varepsilon(t))_{t\in\mathbb{R}}$, we obtain for the first term on the right hand side of the above inequality (and analogously for the third one)

$$\begin{aligned} |\, f^\varepsilon_{\psi_0^\varepsilon}(s) - f^\varepsilon_{\psi}(s)\,| &\le \left|\left\langle \psi_0^\varepsilon - \psi, U^\varepsilon(-s)(\Pi^\pm a_\varepsilon\Pi^\pm)(q,-i\varepsilon\nabla_q)U^\varepsilon(s)\psi_0^\varepsilon\right\rangle_{L^2(\mathbb{R}^2)}\right| \\ &+ \left|\left\langle \psi, U^\varepsilon(-s)(\Pi^\pm a_\varepsilon\Pi^\pm)(q,-i\varepsilon\nabla_q)U^\varepsilon(s)(\psi-\psi_0^\varepsilon)\right\rangle_{L^2(\mathbb{R}^2)}\right| \\ &\le \text{const.}\,\|\psi_0^\varepsilon - \psi\|_{L^2(\mathbb{R}^2)}\left(\|\psi_0^\varepsilon\|_{L^2(\mathbb{R}^2)} + \|\psi\|_{L^2(\mathbb{R}^2)}\right), \end{aligned}$$

while for the second term we have by the bound on the first derivative

$$|\, f^\varepsilon_\psi(s) - f^\varepsilon_\psi(t)\,| \le \text{const.}\,|s-t|\,.$$

Thus, regardless of the choice of initial data, the sequence $(f^{\varepsilon}_{\psi^{\varepsilon}_0})_{\varepsilon>0}$ is pointwise bounded and equicontinuous. By the Arzela-Ascoli Theorem, we then have uniform convergence of a subsequence on compact subsets of $\mathbb{R}$, which shows the claimed uniform convergence on intervals $[0,T]$ for all $T>0$.

As the second step, we prove that the two-scale limits define positive bounded scalar-valued Radon measures $\rho^{\pm}_t$ for all $t\in[0,T]$. Clearly, the limits define linear forms on the space of functions in $\mathcal{A}$ with support away from $\{q=0\}$. By the standard arguments, which have already been invoked in the proof of Proposition 6, they extend to linear forms on compactly supported continuous functions on $\mathbb{R}^4\times\overline{\mathbb{R}}$ with support away from $\{q=0\}$. Such functions, however, are dense with respect to the sup-norm in $C_c((\mathbb{R}^4\setminus\{q=0\})\times\overline{\mathbb{R}},\mathbb{C})$, and we obtain the measures $\rho^{\pm}_t$ on $(\mathbb{R}^4\setminus\{q=0\})\times\overline{\mathbb{R}}$.

As the third step, we show the asserted transport properties. Omitting the subscript ψ^{ε}_0 of the function $f^{\varepsilon}_{\psi^{\varepsilon}_0}$ for notational simplicity, we have for scalar-valued observables $a\in\mathcal{A}$ with support away from $\{q=0\}$

$$\lim_{k\to\infty}\left\langle W^{\varepsilon_k}_2(\psi^{\varepsilon_k}(t)),a\,\Pi^{\pm}\right\rangle_{\mathcal{A}',\mathcal{A}} \;=\; \lim_{k\to\infty} f^{\varepsilon_k}(t)$$

uniformly in $t\in[0,T]$. As already noted, the above uniform limit defines a measure $\rho^{\pm}_t$ on $(\mathbb{R}^4\setminus\{q=0\})\times\overline{\mathbb{R}}$ for all $t\in[0,T]$. For initial data $\psi^{\varepsilon}_0\in D(H^{\varepsilon})$, the function $t\mapsto f^{\varepsilon}(t)$ is continuously differentiable with a first order derivative, whose leading order term in ε is given by the commutator expression in equation (50). Thus,

$$\begin{aligned}
&\lim_{k\to\infty}\tfrac{d}{dt}f^{\varepsilon_k}(t)\\
&\;=\;\lim_{k\to\infty}\left\langle(\phi\Pi^{\pm})(q,-i\varepsilon_k\nabla_q)\psi^{\varepsilon_k}(t),(\{\lambda^{\pm}_0,a\})_{\varepsilon_k}(q,-i\varepsilon_k\nabla_q)(\phi\Pi^{\pm})(q,-i\varepsilon_k\nabla_q)\psi^{\varepsilon_k}(t)\right\rangle_{L^2}\\
&\;=\;\lim_{k\to\infty}\left\langle W^{\varepsilon_k}_2(\psi^{\varepsilon_k}(t)),\{\lambda^{\pm}_0,a\}\Pi^{\pm}\right\rangle_{\mathcal{A}',\mathcal{A}} \;=\; \int\{\lambda^{\pm}_0,a\}(q,p,\eta)\,\rho^{\pm}_t(dq,dp,d\eta)\,.
\end{aligned}$$

On the other hand, by the uniform convergence of $(f^{\varepsilon_k}(t))_{k\in\mathbb{N}}$,

$$\begin{aligned}
&\lim_{k\to\infty}\tfrac{d}{dt}f^{\varepsilon_k}(t) \;=\; \tfrac{d}{dt}\lim_{k\to\infty}f^{\varepsilon_k}(t) \;=\\
&\qquad\tfrac{d}{dt}\lim_{k\to\infty}\left\langle W^{\varepsilon_k}_2(\psi^{\varepsilon_k}(t)),a\,\Pi^{\pm}\right\rangle_{\mathcal{A}',\mathcal{A}} \;=\; \tfrac{d}{dt}\int a(q,p,\eta)\,\rho^{\pm}_t(dq,dp,d\eta)\,,
\end{aligned}$$

which implies

$$\tfrac{d}{dt}\rho^{\pm}_t \;=\; -\{\lambda^{\pm}_0,\rho_t\}$$

for $t\in[0,T]$ such that $\bigcup_{j\in\{\pm\}}\{\Phi^t_j(q,p)\mid\exists\eta\in\overline{\mathbb{R}}:(q,p,\eta)\in\mathrm{supp}(\rho_0)\}\cap\{q=0\} \;=\; \emptyset$, or equivalently $\rho^{\pm}_t(q,p,\eta)=\rho^{\pm}_0(\Phi^t_{\pm}(q,p),\eta)$, or

$$\lim_{k\to\infty}\left\langle W^{\varepsilon_k}(\psi^{\varepsilon_k}(t))-W^{\varepsilon_k}(\psi^{\varepsilon_k}_0)\circ\Phi^{-t}_{\pm},a\,\Pi^{\pm}\right\rangle_{\mathcal{A}',\mathcal{A}} \;=\; 0\,.$$

The assumption on the measure ρ_0 guarantees that the sequences $(\langle W^{\varepsilon}_2(\psi^{\varepsilon}_0),a\,\Pi^{\pm}\rangle)_{\varepsilon>0}$ converge to measures $\rho^{\pm}_0$ without extraction of subsequences. Thus, every convergent subsequence of $(\langle W^{\varepsilon}_2(\psi^{\varepsilon}(t)),a\,\Pi^{\pm}\rangle)_{\varepsilon>0}$ converges to the same limit point, and therefore the whole sequence itself has to converge. Observing that

$$L^2(\mathbb{R}^2,\mathbb{C}^2)\times L^2(\mathbb{R}^2,\mathbb{C}^2)\to\mathbb{C}\,,\qquad (f,g)\mapsto\langle U^{\varepsilon}(t)f,a_{\varepsilon}(q,-i\varepsilon\nabla_q)\,U^{\varepsilon}(t)g\rangle_{L^2(\mathbb{R}^2)}$$

is a bounded bilinear form, we conclude the proof of the transport equation also for the case of general initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ by a density argument. $\square$

The previous Proposition 7 also shows for the Wigner measures $\mu_t^\pm$, that $\mu_t^\pm = \mu_0^\pm \circ \Phi_\pm^{-t}$ on time intervals $[0, T]$ such that for all $t \in [0, T]$

$$\bigcup_{j \in \{\pm\}} \{\Phi_j^t(q,p) \mid (q,p) \in \mathrm{supp}(\rho_0)\} \cap \{q = 0\} \;=\; \emptyset\,.$$

Since $\Phi_\pm^t$ leaves $I = \{q \wedge p = 0\}$ invariant,

$$\mu_t^\pm\,|_{\mathbb{R}^4\setminus I} = \;(\mu_0^\pm \circ \Phi_\pm^{-t})\,|_{\mathbb{R}^4\setminus I} \tag{51}$$

for all times $t \in \mathbb{R}$. While the diagonal components of a two-scale Wigner functional approximately satisfy classical transport equations, its off-diagonal elements vanish when taking time averages.

LEMMA 11 (VANISHING COMMUTATOR) *Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ be the solution of the Schrödinger equation (1) with arbitrary initial datum $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. Then, for all $a \in \mathcal{A}$ and all $t_1, t_2 \in \mathbb{R}$ there exists a positive constant $C = C(a, V, t_1, t_2) > 0$ depending on a, V, t_1, and t_2 such that for all $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$*

$$\Big|\int_{t_1}^{t_2} \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), [V, a]\,\rangle_{\mathcal{A}',\mathcal{A}}\, d\tau\,\Big| \le\; \sqrt{\varepsilon}\; C\; \|\psi_0^\varepsilon\|^2_{L^2(\mathbb{R}^2)}\,.$$

PROOF. Let $\psi_0^\varepsilon \in D(H^\varepsilon)$ and $a \in \mathcal{A}$. We have for all $\tau \in \mathbb{R}$

$$i\varepsilon\, \tfrac{d}{d\tau}\, \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), a\,\rangle_{\mathcal{A}',\mathcal{A}} \;=\; \langle \psi^\varepsilon(\tau), [H^\varepsilon, a_\varepsilon(q, -i\varepsilon\nabla_q)]\,\psi^\varepsilon(\tau)\rangle_{L^2(\mathbb{R}^2)}\,.$$

Thus, we analyze the commutator $[H^\varepsilon, a_\varepsilon(q, -i\varepsilon\nabla_q)] = [h, a_\varepsilon]_{\sharp_\varepsilon}(q, -i\varepsilon\nabla_q)$. Since a is Schwartz function, we have $a_\varepsilon \in S^0_{1/2}(\langle q\rangle^{-1}\langle p\rangle^{-2})$, and applying Lemma 5 we obtain $[h, a_\varepsilon]_{\sharp_\varepsilon} - [h, a_\varepsilon] =: \sqrt{\varepsilon}\, r^\varepsilon \in S^{-1/2}_{1/2}(1)$. Thus, with $[h, a_\varepsilon] = [V, a_\varepsilon]$,

$$\begin{aligned} &i\varepsilon\, \tfrac{d}{d\tau}\, \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), a\,\rangle_{\mathcal{A}',\mathcal{A}} \;=\\ &\qquad \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), [h, a]\,\rangle_{\mathcal{A}',\mathcal{A}} + \sqrt{\varepsilon}\; \langle \psi^\varepsilon(\tau), r^\varepsilon(q, -i\varepsilon\nabla_q)\,\psi^\varepsilon(\tau)\rangle_{L^2(\mathbb{R}^2)}\,. \end{aligned} \tag{52}$$

Integration from t_1 to t_2 gives

$$\begin{aligned} \varepsilon\,\Big|\int_{t_1}^{t_2} \tfrac{d}{d\tau}\, \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), a\,\rangle_{\mathcal{A}',\mathcal{A}}\, d\tau\,\Big| \;&=\; \varepsilon\,|\,\langle W_2^\varepsilon(\psi^\varepsilon(t_2)) - W_2^\varepsilon(\psi^\varepsilon(t_1)), a\,\rangle_{\mathcal{A}',\mathcal{A}}\,| \\ &\le\; \varepsilon\; s_5(a)\; \|\psi_0^\varepsilon\|^2_{L^2(\mathbb{R}^2)} \end{aligned}$$

and

$$\sqrt{\varepsilon}\;\Big|\int_{t_1}^{t_2} \langle \psi^\varepsilon(\tau), r^\varepsilon(q, -i\varepsilon\nabla_q)\,\psi^\varepsilon(\tau)\rangle_{L^2(\mathbb{R}^2)}\, d\tau\,\Big| \le\; \sqrt{\varepsilon}\; c_4(r^\varepsilon)\; |t_1 - t_2|\; \|\psi_0^\varepsilon\|^2_{L^2(\mathbb{R}^2)}\,,$$

which together with equation (52) yields the claimed bound for $\psi_0^\varepsilon \in D(H^\varepsilon)$. A density argument concludes the proof also for general initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$. $\square$

REMARK 17 The previous proof also applies to general matrix-valued Schrödinger equations with essentially self-adjoint Hamiltonian, whose symbol is polynomially bounded, and to two-scaled Wigner functionals associated with more general submanifolds than the hypersurface of zero angular momentum $I = \{q \wedge p = 0\}$. $\diamondsuit$

Purely off-diagonal symbols $a \in \mathcal{A}$ with $\mathrm{supp}(a) \cap \{q = 0\} = \emptyset$ can be written as $a = \Pi^+ a \Pi^- + \Pi^- a \Pi^+$, which implies $[V, a] = (\lambda_0^+ - \lambda_0^-)a$ and $a = [V, (\lambda_0^+ - \lambda_0^-)^{-1} a]$. Thus, we have for such off-diagonal observables

$$| \int_{t_1}^{t_2} \langle W_2^\varepsilon(\psi^\varepsilon(\tau)), a \rangle_{\mathcal{A}', \mathcal{A}} \, d\tau \, | \leq \sqrt{\varepsilon} \, C \, \|\psi_0^\varepsilon\|_{L^2(\mathbb{R}^2)}^2 .$$

12.4 MEASURES ON $\mathbb{R}^2_{t,\tau} \times \mathbb{R}^4_{q,p} \times \overline{\mathbb{R}}_\eta$

We fix some time-interval of interest $[0, T]$ with $T > 0$ and define a set of admissible observables on an extended phase space $[0, T]_t \times \mathbb{R}_\tau \times \mathbb{R}^4_{q,p}$ as

$$\mathcal{A}_T := \left\{ a \in C_b^\infty(\mathbb{R}^7, \mathcal{L}(\mathbb{C}^2)) \mid a \text{ satisifes property } (\mathbf{P_T}) \right\},$$

where

$(\mathbf{P_T})$ $\quad \mathrm{supp}(a) \subset [0, T] \times \mathbb{R}^6$ and $a(t, \tau, \cdot) \in \mathcal{A}$ for all $t, \tau \in \mathbb{R}$.

For $a \in \mathcal{A}_T$ we set

$$a_\varepsilon(t, q, \tau, p) =: a(t, q, \tau, p, \tfrac{q \wedge p}{\sqrt{\varepsilon}}) .$$

and choose a cut-off function $\chi_T \in C_c^\infty(\mathbb{R}, \mathbb{R})$ such that $\chi_T(t) = 1$ for $t \in [0, T]$. Then, we define for $\psi \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$

$$W_{2,T}^\varepsilon(\psi) : \quad \mathcal{A}_T \to \mathbb{C}, \quad a \mapsto \langle \chi_T \psi, a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) \chi_T \psi \rangle_{L^2(\mathbb{R}^3)} ,$$

which is a bounded linear functional by the rescaling identity (44) already used before. The alternative approach followed up in [FeGe1] applies to observables $a \in \mathcal{S}(\mathbb{R}^7, \mathcal{L}(\mathbb{C}^2))$ and treats $\psi \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ as a temperate distribution on $\mathbb{R}^3$. Then, $a_\varepsilon \in \mathcal{S}(\mathbb{R}^6, \mathcal{L}(\mathbb{C}^2))$, and the Weyl quantized operator is regularizing, that is

$$a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) \in \mathcal{L}(\mathcal{S}'(\mathbb{R}^3, \mathbb{C}^2), \mathcal{S}(\mathbb{R}^3, \mathbb{C}^2)) ,$$

see Remark 4 in Part B. For symbols $a \in \mathcal{A}_T \cap \mathcal{S}(\mathbb{R}^7, \mathcal{L}(\mathbb{C}^2))$ we have by Lemma 5

$$\chi_T \sharp_\varepsilon a_\varepsilon \sharp_\varepsilon \chi_T \sim a_\varepsilon \quad \text{in} \quad S^0_{1/2}(1) ,$$

and therefore

$$a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) = \chi_T \, a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) \, \chi_T \in \mathcal{L}(\mathcal{S}'(\mathbb{R}^3, \mathbb{C}^2), \mathcal{S}(\mathbb{R}^3, \mathbb{C}^2)) .$$

Consequently,

$$\langle \chi_T \psi, a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) \chi_T \psi \rangle_{L^2(\mathbb{R}^3)} = \left\langle \overline{\psi}, a_\varepsilon(t, q, -i\varepsilon \nabla_{t,q}) \psi \right\rangle_{\mathcal{S}', \mathcal{S}} .$$

For different cut-off functions χ_T, $\widetilde{\chi}_T \in C_c^\infty(\mathbb{R},\mathbb{R})$ with $\chi_T(t) = \widetilde{\chi}_T(t) = 1$ for $t \in [0,T]$, we have

$$\chi_T \sharp_\varepsilon a_\varepsilon \sharp_\varepsilon \chi_T \sim \widetilde{\chi}_T \sharp_\varepsilon a_\varepsilon \sharp_\varepsilon \widetilde{\chi}_T \quad \text{in} \quad S^0_{1/2}(1)\,,$$

and thus the independence of $\mathcal{W}^\varepsilon_{2,T}(\psi)$ from the choice of the cut-off function. Balancing the benefits of the two equivalent approaches of using a cut-off function in $L^2(\mathbb{R}^3)$ versus working with temperate distributions, we have preferred the natural setting of L^2-theory.

For $(\psi^\varepsilon)_{\varepsilon>0}$ in $C(\mathbb{R}, L^2(\mathbb{R}^2,\mathbb{C}^2))$ with $\sup_{\varepsilon>0,t\in\mathbb{R}} \|\psi^\varepsilon(t)\|_{L^2(\mathbb{R}^2)} < \infty$, the sequence of two-scale functionals $(\mathcal{W}^\varepsilon_{2,T}(\psi^\varepsilon))_{\varepsilon>0}$ has weak*-limit points ρ_T in $\mathcal{A}'_T$, which are bounded positive matrix-valued Radon measures on $[0,T]\times\mathbb{R}^5\times\overline{\mathbb{R}}$. As before, we denote by ν_T the restriction of a measure ρ_T to the set $\{(t,q,\tau,p,\eta) \in [0,T]\times\mathbb{R}^5\times\overline{\mathbb{R}} \mid (q,p) \in I\}$. The following lemma addresses the localization of the measures ρ_T on the energy shell. The analogous statement for semi-classical measures has been given in Section 3 of [Ge2].

Lemma 12 (Localization) *Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2,\mathbb{C}^2))$ be the solution of the model problem (1), whose initial data $(\psi_0^\varepsilon)_{\varepsilon>0}$ form a bounded sequence in $L^2(\mathbb{R}^2,\mathbb{C}^2)$. Then, we have for the weak*-limit points $\rho_T \in \mathcal{A}'_T$ of $(W^\varepsilon_{2,T}(\psi^\varepsilon))_{\varepsilon>0}$*

$$\mathrm{supp}(\rho_T) \subset \left\{(t,\tau,q,p,\eta) \in [0,T]\times\mathbb{R}^5\times\overline{\mathbb{R}} \;\mid\; \tau + \tfrac{1}{2}|p|^2 = \pm|q|\right\}.$$

Proof. We define a linear operator

$$\widetilde{H}^\varepsilon \;:=\; -i\varepsilon\partial_t - H^\varepsilon \;=\; (\tau+h)((t,q),-i\varepsilon\nabla_{t,q})$$

with domain

$$D(\widetilde{H}^\varepsilon) \;:=\; \{\psi \in L^2(\mathbb{R}^3,\mathbb{C}^2) \mid \psi(\cdot,q) \in C^1(\mathbb{R},\mathbb{C}^2) \;\text{ for } q \in \mathbb{R}^2\,, \psi(t,\cdot) \in D(H^\varepsilon) \text{ for } t \in \mathbb{R}\}.$$

For initial data $\psi_0^\varepsilon \in D(H^\varepsilon)$ the solution ψ^ε is in $C^1(\mathbb{R}, D(H^\varepsilon))$. Thus, $\chi_T\psi^\varepsilon \in D(\widetilde{H}^\varepsilon)$ and

$$\|\widetilde{H}^\varepsilon(\chi_T\psi^\varepsilon)\|_{L^2(\mathbb{R}^3)} \;=\; \|(-i\varepsilon\partial_t\chi_T)\,\psi^\varepsilon\|_{L^2(\mathbb{R}^3)} \;\overset{\varepsilon\to 0}{\longrightarrow}\; 0\,.$$

The symbol a_ε need not have any decay properties for large τ. However, since $\tau+h$ is linear in τ, the reasoning of Lemma 5's proof gives for $a \in \mathcal{A}_T$

$$a_\varepsilon \sharp_\varepsilon (\tau+h) - a_\varepsilon(\tau+h) \in S^{-1/2}_{1/2}(1)\,.$$

For a well-defined pairing with ρ_T, we restrict ourselves to symbols $a \in \mathcal{A}_T$ with support $\mathrm{supp}(a) \subset [0,T]\times\mathbb{R}^2_q\times[\tau_1,\tau_2]\times\mathbb{R}^3_{p,\eta}$ for some $\tau_1,\tau_2 \in \mathbb{R}$ and have

$$\begin{aligned}
\langle\, \rho_T, a(\tau+h)\,\rangle_{\mathcal{A}'_T,\mathcal{A}_T} \;&=\; \lim_{k\to\infty} \langle \chi_T\psi^{\varepsilon_k}, (a_\varepsilon(\tau+h))((t,q),-i\varepsilon_k\nabla_{t,q})\,(\chi_T\psi^{\varepsilon_k})\rangle_{L^2(\mathbb{R}^3)} \\
&=\; \lim_{k\to\infty} \left\langle \chi_T\psi^{\varepsilon_k}, a_\varepsilon((t,q),-i\varepsilon_k\nabla_{t,q})\,\widetilde{H}^{\varepsilon_k}(\chi_T\psi^{\varepsilon_k})\right\rangle_{L^2(\mathbb{R}^3)} \;=\; 0\,.
\end{aligned}$$

Since ρ_T is a distribution of order zero, and since the set of symbols used in the preceding lines is dense in $C_c(\mathbb{R}^6\times\overline{\mathbb{R}}, \mathcal{L}(\mathbb{C}^2))$, we have $\rho_T(\tau+h) = 0$ as measures, provided initial data $\psi_0^\varepsilon \in D(H^\varepsilon)$. A $\|\cdot\|_{L^2(\mathbb{R}^2)}$-density argument proves

$$\langle \rho_T, a(\tau+h)\rangle_{\mathcal{A}'_T,\mathcal{A}_T} \;=\; 0$$

for general initial data $\psi_0^\varepsilon \in L^2(\mathbb{R}^2,\mathbb{C}^2)$ and observables $a \in \mathcal{A}_T$ with compact τ-support, while another $\|\cdot\|_\infty$-density argument gives $\rho_T(\tau+h) = 0$ in the sense of measures. Observing that $V(q)^2 = |q|^2\,\mathrm{Id}$, we finally obtain the claimed assertion on the support of ρ_T. □

It remains to clarify the relation between two-scale measures on $\mathbb{R}^4_{q,p} \times \overline{\mathbb{R}}_\eta$ and their pendant on $\mathbb{R}^2_{t,\tau} \times \mathbb{R}^4_{q,p} \times \overline{\mathbb{R}}_\eta$.

Lemma 13 *Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2,\mathbb{C}^2))$ be the solution of the Schrödinger equation (1) with initial data $(\psi_0^\varepsilon)_{\varepsilon>0}$ bounded in $L^2(\mathbb{R}^2,\mathbb{C}^2)$. Let ρ_T be a weak*-limit point of $(W^\varepsilon_{2,T}(\psi^\varepsilon))_{\varepsilon>0}$, and let $\rho_t^\pm$ be the scalar measures introduced in Proposition 7. Then,*

$$\left\langle \rho_T, \Pi^\pm\, a\, \Pi^\pm \right\rangle_{\mathcal{A}_T',\mathcal{A}_T} \;=\; \int_{\mathbb{R}^6\times\overline{\mathbb{R}}} a^\pm(t,q,\tau,p,\eta)\, \rho_t^\pm(dq,dp,d\eta)\, \delta(\tau - \tfrac{1}{2}|p|^2 \mp |q|)\, dt$$

for all $a \in \mathcal{A}_T$ with $\mathrm{supp}(a) \subset [-T,T]\times\mathbb{R}^6 \setminus \{q=0\}$ *and* $a^\pm = \mathrm{tr}(a\Pi^\pm)$.

Proof. Let $(\varepsilon_k)_{k\in\mathbb{N}}$ be a subsequence, such that

$$W^{\varepsilon_k}_{2,T}(\psi^{\varepsilon_k}) \stackrel{*}{\rightharpoonup} \rho_T\,, \qquad \mathrm{tr}\left(W_2^{\varepsilon_k}(\psi^{\varepsilon_k}(t))\Pi^\pm\right) \stackrel{*}{\rightharpoonup} \rho_t^\pm \quad \text{uniformly in} \quad t\in[0,T]\,.$$

Since $\rho_T\,(\tau + \frac{1}{2}|p|^2 + V) = 0$ and therefore $\mathrm{supp}(\mathrm{tr}(\rho_T\Pi^\pm)) \subset \{\tau + \frac{1}{2}|p|^2 \pm |q| = 0\}$, we have

$$\mathrm{tr}\left(\rho_T(t,q,\tau,p,\eta)\,\Pi^\pm(q)\right) \;=\; \int_{\mathbb{R}} \mathrm{tr}\left(\rho_T(t,q,d\tau,p,\eta)\,\Pi^\pm(q)\right)\, \delta(\tau + \tfrac{1}{2}|p|^2 \pm |q|)$$

as measures on $[0,T]\times(\mathbb{R}^2_q\setminus\{0\})\times\mathbb{R}^3_{\tau,p}\times\overline{\mathbb{R}}_\eta$. Thus, it remains to show that

$$\rho_t^\pm(q,p,\eta) \;=\; \int_{\mathbb{R}} \mathrm{tr}\left(\rho_T(t,q,d\tau,p,\eta)\,\Pi^\pm(q)\right)$$

as measures on $[0,T]\times(\mathbb{R}^2_q\setminus\{0\})\times\mathbb{R}^2_p\times\overline{\mathbb{R}}_\eta$. We have for symbols $a = a(t,q,p,\eta) \in \mathcal{A}_T$, which do not depend on τ and have support away from $\{q=0\}$,

$$\begin{aligned}
&\int_{\mathbb{R}^6\times\overline{\mathbb{R}}} \mathrm{tr}\left(a(t,q,p,\eta)\,\Pi^\pm(q)\right)\; \rho_T^\pm(dt,dq,d\tau,dp,d\eta) \\
&= \lim_{k\to\infty} \left\langle \chi_T\psi^{\varepsilon_k}, (\Pi^\pm a_\varepsilon \Pi^\pm)(t,q,-i\varepsilon_k\nabla_q)\chi_T\psi^{\varepsilon_k}\right\rangle_{L^2(\mathbb{R}^3,\mathbb{C}^2)} \\
&= \lim_{k\to\infty} \int_{\mathbb{R}} |\chi_T(t)|^2 \left\langle \psi^{\varepsilon_k}(t), (\Pi^\pm a_\varepsilon \Pi^\pm)(t,q,-i\varepsilon_k\nabla_q)\psi^{\varepsilon_k}(t)\right\rangle_{L^2(\mathbb{R}^2,\mathbb{C}^2)}\, dt \\
&= \int_{\mathbb{R}^5\times\overline{\mathbb{R}}} \mathrm{tr}\left(a(t,q,p,\eta)\Pi^\pm\right)\; \rho_t^\pm(dq,dp,d\eta)\, dt\,,
\end{aligned}$$

which concludes our proof. □

12.5 The Results of Fermanian and Gérard

In the following, we summarize the part of the results of [FeGe1], which we will use for the proof of Theorem 8. In [FeGe1], C. Fermanian and P. Gérard have considered the system

$$i\,\varepsilon\,\partial_t\psi^\varepsilon \;=\; H^\varepsilon_{FG}\,\psi^\varepsilon\,, \qquad \psi^\varepsilon(0) \;=\; \psi_0^\varepsilon \in L^2(\mathbb{R}^2,\mathbb{C}^2) \tag{53}$$

with Hamiltonian

$$H^\varepsilon_{FG} \;=\; k(x) + \begin{pmatrix} -i\varepsilon\partial_{x_1} & -i\varepsilon\partial_{x_2} \\ -i\varepsilon\partial_{x_2} & i\varepsilon\partial_{x_1} \end{pmatrix} \;=\; k(x) + V(-i\varepsilon\nabla_x)\,,$$

where $k \in C^\infty(\mathbb{R}^2, \mathbb{R})$ is a smooth real-valued function. If $k(x) = \frac{1}{2}|x|^2$, then conjugation by the ε-scaled Fourier transform $\mathcal{F}_\varepsilon$ gives unitary equivalence to the model Hamiltonian H^ε,

$$H^\varepsilon \;=\; \mathcal{F}_\varepsilon\, H^\varepsilon_{FG}\, \mathcal{F}^*_\varepsilon\,.$$

The crossing asscociated with H^ε_{FG} is in momentum space at $\xi = 0$. Proposition 4 in [FeGe1] shows existence of a function $\omega : \mathbb{R}^3 \to \mathbb{R}^2$ with $|\omega(\tau, x)| = 1$ for all $(\tau, x) \in \mathbb{R}^3$ such that

$$I_{FG} = \left\{(t, \tau, x, \xi) \in \mathbb{R}^6 \mid \omega(\tau, x) \wedge \xi = 0\right\}, \tag{54}$$

is an involutive submanifold, which for some point $(t_0, \tau_0, x_0, 0) \in \mathbb{R}^6$ contains the classical trajectories associated with the eigenvalues of the symbol $k(x) + V(\xi)$, which are issued in a neighborhood $U \in \mathbb{R}^6$ of the point $(t_0, \tau_0, x_0, 0)$. The space of admissible observables is chosen as

$$\begin{aligned}\mathcal{A}_{FG} := \big\{a \in C^\infty(\mathbb{R}^7, \mathcal{L}(\mathbb{C}^2)) \mid \operatorname{supp}(a) \subset K \times \mathbb{R}\,,\ K \subset \mathbb{R}^6 \text{ compact}\,,\\ \exists\, a_\infty \in C^\infty(\mathbb{R}^6 \times \{\pm 1\}, \mathcal{L}(\mathbb{C}^2))\ \exists\, R > 0\ \forall\, m \in \mathbb{R}^6\ \forall |\eta| > R :\\ a(m, \eta) = a_\infty(m, \operatorname{sgn}(\eta))\big\}\,.\end{aligned}$$

Theorem 1 of [FeGe1] shows, that for a bounded sequence $(u^\varepsilon)_{\varepsilon>0}$ in $L^2(\mathbb{R}^3, \mathbb{C}^2)$ there exists a subsequence $(\varepsilon_k)_{k>0}$ of positive numbers and a positive Radon measure ν_{FG} on $I_{FG} \times \overline{\mathbb{R}}$ with values in $\mathcal{L}_{sa}(\mathbb{C}^2)$ such that for all $a \in \mathcal{A}_{FG}$

$$\begin{aligned}\lim_{\varepsilon_k \to 0} \int_{\mathbb{R}^4} \operatorname{tr}\Big(W^{\varepsilon_k}(u^{\varepsilon_k})(t, \tau, q, p)\, a\big(t, \tau, x, \xi, \tfrac{\omega(x,\tau)\wedge\xi}{\sqrt{\varepsilon_k}}\big)\Big)\, dt\, d\tau\, dx\, d\xi \;=\\ \int_{I_{FG}\times\overline{\mathbb{R}}} \operatorname{tr}\left(a(t, \tau, x, \xi, \eta)\, \nu_{FG}(dt, d\tau, dx, d\xi, d\eta)\right)\\ + \int_{\mathbb{R}^6\setminus I_{FG}} \operatorname{tr}\left(a_\infty\left(t, \tau, x, \xi, \operatorname{sgn}(\omega(x,\tau) \wedge \xi)\right) \mu(dt, d\tau, dx, d\xi)\right)\,,\end{aligned}$$

where $(W^\varepsilon(u^\varepsilon))_{\varepsilon>0}$ and μ are Wigner transforms and a Wigner measure of $(u^\varepsilon)_{\varepsilon>0}$, respectively. Theorem 2' of [FeGe1] associates with the solution $\psi^\varepsilon(t, x)$ of (53) a measure ν_{FG} on $\mathbb{R}^6 \times \overline{\mathbb{R}}$, which decomposes as

$$\nu_{FG} \;=\; \nu^+_{FG}\,\Pi^+ \,+\, \nu^-_{FG}\,\Pi^-$$

with scalar measures $\nu^\pm_{FG}$ supported in $J^{\pm,p} \cup J^{\pm,f}$. For the definition of the sets $J^{\pm,p}$ and $J^{\pm,f}$, C. Fermanian and P. Gèrard restrict the crossing manifold $\{\xi = 0\}$ to the set

$$S_{FG} \;:=\; \left\{(t, \tau, x, 0, \eta) \in \mathbb{R}^6 \times \overline{\mathbb{R}} \mid t \in \mathbb{R},\ \tau = -k(x),\ x \neq 0,\ \eta \in \overline{\mathbb{R}}\right\},$$

choose a point $(t_0, \tau_0, x_0, 0, \eta_0) \in S_{FG}$ and a neighborhood $(t_0, \tau_0, x_0, 0) \in U \subset \mathbb{R}^6$, and define

$$\begin{aligned} J^{\pm,p} &:= \left\{(t+s, \tau, \Phi^s_{FG,\pm}(x,0), \eta) \in \mathbb{R}^6 \times \overline{\mathbb{R}} \mid (t,\tau,x,0) \in U\,,\ s<0 \text{ sufficiently small}\right\}, \\ J^{\pm,f} &:= \left\{(t+s, \tau, \Phi^s_{FG,\pm}(x,0), \eta) \in \mathbb{R}^6 \times \overline{\mathbb{R}} \mid (t,\tau,x,0) \in U\,,\ s>0 \text{ sufficiently small}\right\}, \end{aligned}$$

where $\Phi^t_{FG,\pm}$ are the classical flows associated with the Hamiltonian systems

$$\dot{x} \;=\; \mp \tfrac{\xi}{|\xi|}\,, \qquad \dot{\xi} \;=\; \nabla k(x)\,.$$

By Theorem 2' in [FeGe1], the measures $\nu^{\pm}_{FG}$ satisfy the transport equations

$$\partial_t \nu^{\pm}_{FG} \;\pm\; \tfrac{\xi}{|\xi|}\cdot\nabla_x \nu^{\pm}_{FG} \;-\; \nabla k(x)\cdot\nabla_\xi \nu^{\pm}_{FG} \;\pm\; (\nabla\cdot\omega)\,\partial_\eta(\eta\,\nu^{\pm}_{FG}) \;=\; 0\,,$$

on $J^{\pm,p} \setminus S_{FG}$ and

$$\partial_t \nu^{\pm}_{FG} \;\pm\; \tfrac{\xi}{|\xi|}\cdot\nabla_x \nu^{\pm}_{FG} \;-\; \nabla k(x)\cdot\nabla_\xi \nu^{\pm}_{FG} \;\mp\; (\nabla\cdot\omega)\,\partial_\eta(\eta\,\nu^{\pm}_{FG}) \;=\; 0\,,$$

on $J^{\pm,f} \setminus S_{FG}$. Denoting restrictions of the measures $\nu^{\pm}_{FG}$ to $J^{\pm,p} \cap S_{FG}$ and $J^{\pm,f} \cap S_{FG}$ by $\nu^{\pm,p}_{S_{FG}}$ and $\nu^{\pm,f}_{S_{FG}}$, respectively, Theorem 3 of [FeGe1] shows the Landau-Zener type formula

$$\begin{pmatrix} \nu^{+,f}_{S_{FG}} \\ \nu^{-,f}_{S_{FG}} \end{pmatrix} \;=\; \begin{pmatrix} 1-T_{FG} & T_{FG} \\ T_{FG} & 1-T_{FG} \end{pmatrix} \begin{pmatrix} \nu^{+,p}_{S_{FG}} \\ \nu^{-,p}_{S_{FG}} \end{pmatrix}$$

with

$$T_{FG} \;=\; T_{FG}(x,\eta) \;=\; \exp\Big(-\pi\,\tfrac{\eta^2}{|\nabla k(x)|}\Big)\,,$$

if $\nu^{+,p}_{S_{FG}}$ and $\nu^{-,p}_{S_{FG}}$ are mutually singular on S_{FG}. A sufficient condition to meet this singularity requirement for positive times $t \geq 0$ is the choice of initial data $\psi^\varepsilon_0 \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ with $\Pi^- \psi^\varepsilon_0 \;=\; 0$, since then

$$\nu^{-,p}_{S_{FG}}\big|_{\{t\geq 0\}} \;\equiv\; 0\,.$$

The proof of the above Landau-Zener formula reduces the system (53) to a scattering problem, which is close to the purely time-dependent Landau-Zener system (40). The reduction is achieved by a change of symplectic time-space coordinates $(t,\tau,x,\xi) \mapsto (s,\sigma,z,\zeta)$, such that *microlocally* in the new coordinates

$$J^{\pm,p} \;\overset{\text{loc.}}{=}\; \left\{\sigma \pm s = 0,\ \ \zeta_2 = 0,\ \ s<0\right\}, \qquad J^{\pm,f} \;\overset{\text{loc.}}{=}\; \left\{(\sigma \mp s = 0,\ \ \zeta_2 = 0,\ \ s>0\right\}$$

and

$$I_{FG} \;\overset{\text{loc.}}{=}\; \left\{\zeta_2 = 0\right\}, \qquad S_{FG} \;\overset{\text{loc.}}{=}\; \left\{\sigma = s = \zeta_2 = 0\right\}.$$

Up to an error of order ε^2, the system (53) reduces to a normal form

$$i\varepsilon\,\partial_s v^\varepsilon \;=\; Q(s, -i\varepsilon\partial_s, z, -i\varepsilon\nabla_z)\, v^\varepsilon$$

with symbol $Q : \mathbb{R}^6 \to \mathcal{L}(\mathbb{C}^2)$,

$$Q(s,\sigma,z,\zeta) \;\overset{\text{loc.}}{=}\; \begin{pmatrix} s & \alpha(\sigma,z)\zeta_2 \\ \alpha(\sigma,z)\zeta_2 & -s \end{pmatrix},$$

$\alpha : \mathbb{R} \times \mathbb{R}^2 \to \mathbb{R} \setminus \{0\}$ and $\nu^\varepsilon = U^\varepsilon \psi^\varepsilon$, where U^ε is a suitably chosen unitary, matrix-valued Fourier integral operator. Proposition 8 in [FeGe1] removes the σ-dependance of the function α with an error of order $\sqrt{\varepsilon}$, while in the appendix of [FeGe1] the resulting ordinary differential equation is approximately solved by the method of stationary phase. A similar approach yields Landau-Zener type formulae also for codimension three crossings, see [FeGe2]. By an iterative procedure, Y. Colin de Verdiére [CdV] has found microlocal normal forms for symmetric crossings, which come with a superpolynomial error $\mathcal{O}(\varepsilon^\infty)$. Applying C. Fermanian's and P. Gérard's result to the case $k(x) = \frac{1}{2}|x|^2$, we exchange "position and momentum" and switch from (x, ξ) to (q, p). Since the flows $\Phi^t_\pm$ of the Hamiltonian systems (32) conserve angular momentum, the function ω can be chosen as $\omega(\tau, p) = \omega(p) = p$ and I_{FG} can be replaced by

$$\widetilde{I}_{FG} = \left\{(t, \tau, q, p) \in \mathbb{R}^6 \mid q \wedge p = 0\right\}.$$

For the manifold $\widetilde{I}_{FG}$, the same arguments as the ones employed in the proof of Proposition 7 show that the η-derivatives in the transport equations of the two-scale measures drop, and one obtains on $(J^{\pm,p} \cup J^{\pm,f}) \setminus S_{FG}$

$$\widetilde{\nu}^\pm_{FG}(t, \tau, q, p, \eta) = \widetilde{\nu}^\pm_{FG}(0, \tau, \Phi^\pm_t(q, p), \eta).$$

The Landau-Zener transition rate becomes

$$\widetilde{T}_{FG} = \widetilde{T}_{FG}(p, \eta) = \exp\Big(-\pi \tfrac{\eta^2}{|p|^3}\Big).$$

The term $|p|^3$ in $\widetilde{T}_{FG}$ has to be read as $|\nabla k(p)|\,|p|^2$, where the $|p|^2$ stems from the unnormalized choice of the function $\omega(p) = p$, which enforces a transformation in the η-coordinate of the two-scale measures as given in (48).

12.6 A Semigroup for Two-Scale Measures

In complete analogy to the definition of the semigroup $\mathcal{L}^t_\varepsilon$ for the diagonal components $(w^\varepsilon_+(t), w^\varepsilon_-(t))$ of the Wigner function, we define a semigroup for the two-scale Wigner measures (ρ^+_t, ρ^-_t) and (ν^+_t, ν^-_t) associated with the hypersurface of zero angular momentum $I = \left\{(q, p) \in \mathbb{R}^4 \mid q \wedge p = 0\right\}$ in the following. We introduce the right continuous random trajectories

$$\mathcal{J}^{(q,p,\eta,j)} : [0, \infty) \to \mathbb{R}^4 \times \overline{\mathbb{R}}_\eta \times \{-1, 1\},$$

where $\mathcal{J}^{(q,p,\eta,j)}(t) = (\Phi^t_j(q, p), \eta, j)$ as long as $\Phi^t_j(q, p) \notin S$. Whenever the flow $\Phi^t_j(q, p)$ hits the jump manifold S, a jump from j to $-j$ occurs with probability

$$T(p, \eta) = \exp\big(-\pi \tfrac{\eta^2}{|p|^3}\big).$$

The random trajectories $\mathcal{J}^{(q,p,\eta,j)}$ define a Markov process

$$\left\{X^{(q,p,\eta,j)} \mid (q, p, \eta, j) \in \mathbb{R}^4 \times \overline{\mathbb{R}}_\eta \times \{-1, 1\}\right\}.$$

The pendant $\mathcal{C}^2$ to the space of observables $\mathcal{C}$ is defined as follows.

Definition 12 A continuous compactly supported function $f \in C_c((\mathbb{R}^4 \setminus S) \times \overline{\mathbb{R}} \times \{\pm 1\}, \mathbb{C})$ belongs to to the space $\mathcal{C}^2$, if the following boundary conditions at $(S \setminus S_{cl}) \times \overline{\mathbb{R}} \times \{-1, 1\}$ are satisfied:

$$\begin{aligned}
\lim_{\delta \to +0} f(q - \delta p, p - \delta j q/|q|, \eta, j) &= T(p, \eta) \lim_{\delta \to +0} f(q + \delta p, p - \delta j q/|q|, \eta, -j)\,, \\
\lim_{\delta \to +0} f(q - \delta p, p - \delta j q/|q|, \eta, j) &= (1 - T(p, \eta)) \lim_{\delta \to +0} f(q + \delta p, p + \delta j q/|q|, \eta, j)\,.
\end{aligned}$$

By construction of the function space $\mathcal{C}^2$, the semigroup

$$(\mathcal{T}^t f)(q, p, \eta, j) \;:=\; \mathbb{E}^{(q,p,\eta,j)}\, f(\,\mathcal{J}^{(q,p,\eta,j)}(t)\,)\,, \qquad t \geq 0\,,$$

leaves $\mathcal{C}^2$ invariant, that is $\mathcal{T}^t : \mathcal{C}^2 \to \mathcal{C}^2$ for all $t \geq 0$. We denote the space of functions $a \in C_c((\mathbb{R}^4 \setminus S) \times \mathbb{R}, \mathcal{L}(\mathbb{C}^2))$ such that $a = a^+\Pi^+ + a^-\Pi^-$ with $(a^+, a^-) \in \mathcal{C}^2$ by $\mathcal{C}^2_{\rm diag}$ and set for $a \in \mathcal{C}^2_{\rm diag}$

$$\mathcal{T}^t_\pm\, a \;:=\; (\mathcal{T}^t(a^+, a^-))^\pm\,, \qquad \mathcal{T}^t\, a \;:=\; (\mathcal{T}^t_+\, a)\Pi^+ \,+\, (\mathcal{T}^t_-\, a)\Pi^-\,, \qquad t \geq 0\,.$$

We note, that $\mathcal{T}^t$ leaves the space $\mathcal{C}^2_{\rm diag}$ invariant. To work exclusively on the subspaces $\mathrm{Ran}(\Pi^\pm)$, we will also need

$$\mathcal{T}^t_\pm\, a \;:=\; \mathcal{T}^t_\pm(a\,\Pi^\pm)$$

for scalar-valued $a \in C_c((\mathbb{R}^4 \setminus S) \times \overline{\mathbb{R}}, \mathbb{C})$. By duality, we define for matrix-valued Radon measures ρ on $\mathbb{R}^4 \times \overline{\mathbb{R}}$ with $\mathrm{supp}(\rho) \cap (S \times \overline{\mathbb{R}}) = \emptyset$ the matrix-valued measure $\mathcal{T}^t\rho$ on $(\mathbb{R}^4 \setminus S) \times \overline{\mathbb{R}}$, that is, we set

$$\int_{(\mathbb{R}^4 \setminus S) \times \overline{\mathbb{R}}} \mathrm{tr}\left(a(q,p,\eta)\,(\mathcal{T}^t\rho)(dq, dp, d\eta)\right) \;:=\; \int_{\mathbb{R}^4 \times \overline{\mathbb{R}}} \mathrm{tr}\left((\mathcal{T}^t a)(q,p,\eta)\,\rho(dq, dp, d\eta)\right)$$

for $a \in \mathcal{C}^2_{\rm diag}$. Having fixed these notations and definitions, we can formulate the key observation for the proof of Theorem 8.

Lemma 14 *Let $\psi^\varepsilon(t) \in C(\mathbb{R}, L^2(\mathbb{R}^2, \mathbb{C}^2))$ be the solution of the Schrödinger equation (1) with initial data $(\psi^\varepsilon_0)_{\varepsilon > 0}$ bounded in $L^2(\mathbb{R}^2, \mathbb{C}^2)$. Let $T > 0$ and $\rho^\pm_t$, $t \in [0, T]$, be the scalar measures on $(\mathbb{R}^4 \setminus \{q = 0\}) \times \overline{\mathbb{R}}$ introduced in Proposition 7. If*

$$\rho^-_0 = 0 \qquad \textit{and} \qquad \mathrm{supp}(\rho^+_0) \cap (S \times \overline{\mathbb{R}}) = \emptyset\,,$$

then the restrictions $\nu^\pm_t$ of the measures $\rho^\pm_t$ to $I \times \overline{\mathbb{R}}$ satisfy

$$\int_{I \times \overline{\mathbb{R}}} a(q,p,\eta)\, \nu^\pm_t(dq, dp, d\eta) \;=\; \int_{I \times \overline{\mathbb{R}}} (\mathcal{T}^t_\pm a)(q,p,\eta)\, \nu^\pm_0(dq, dp, d\eta)$$

for all scalar-valued $a \in \mathcal{A}$ with $\mathrm{supp}(a) \cap (S \times \overline{\mathbb{R}}) = \emptyset$ and for all $t \in [0, T]$.

Proof. We have to work with measures on $\mathbb{R}^4 \times \overline{\mathbb{R}}$ and on $[0, T] \times \mathbb{R}^5 \times \overline{\mathbb{R}}$ in the following. For all such measures m, which have support away from the jump manifold S, we define the measure $\mathcal{T}^t_\pm\, m$ by

$$\int a(x)\,(\mathcal{T}^t_\pm\, m)(dx) \;:=\; \int (\mathcal{T}^t_\pm\, a)(x)\, m(dx)\,,$$

where the scalar-valued a is either in $\mathcal{A}$ with support away from S or an observable in $\mathcal{A}_T \cap \mathcal{A}_{FG}$ with the same support property. The measure $\mathcal{T}^t_\pm(\nu^\pm_0 \delta(\tau - \lambda^\pm_0)\, dt)$ satisfies the same transport properties and jump conditions at $I \cap S = \{q = 0\}$ as the measure $\nu^\pm_{FG}$. Hence,

$$\mathcal{T}^t_\pm(\nu^\pm_0 \delta(\tau - \lambda^\pm_0)\, dt) \;=\; \nu^\pm_{FG} \qquad \text{on} \qquad \mathcal{A}_T \cap \mathcal{A}_{FG}\,.$$

Since the Hamiltonian flow $\Phi^t_\pm$ conserves energy $\lambda^\pm_0(q,p) = \frac{1}{2}|p|^2 \pm |q|$, and since $\lambda^+_0(q,p) = \lambda^-_0(q,p)$ for $(q,p) \in I \cap S = \{q = 0\}$, we have

$$\mathcal{T}^t_\pm \left(\nu^\pm_0 \delta(\tau - \lambda^\pm_0)\, dt\right) \;=\; \left(\mathcal{T}^t_\pm \nu^\pm_0\right)\, \delta(\tau - \lambda^\pm_0)\, dt \qquad \text{on} \qquad \mathcal{A}_T\,.$$

On the other hand, by Lemma 13

$$\nu^\pm_{FG} \;=\; \nu^\pm_t\, \delta(\tau - \lambda^\pm_0)\, dt \qquad \text{on} \qquad \mathcal{A}_T \cap \mathcal{A}_{FG}\,,$$

and therefore

$$\nu^\pm_t\, \delta(\tau - \lambda^\pm_0)\, dt \;=\; (\mathcal{T}^t_\pm \nu^\pm_0)\, \delta(\tau - \lambda^\pm_0)\, dt \qquad \text{on} \qquad \mathcal{A}_T \cap \mathcal{A}_{FG}\,.$$

By continuity with respect to time t, we then have

$$\nu^\pm_t \;=\; \mathcal{T}^t_\pm\, \nu^\pm_0 \qquad \text{on} \qquad C^\infty_c(\mathbb{R}^5, \mathcal{L}(\mathbb{C}^2))$$

for all times $t \in [0, T]$, and since $\nu^\pm_t$ is a positive distribution, by density the claimed identity on $\mathcal{A}$. □

As an immediate consequence of Lemma 14 we have the following observation of bounded motion on the upper level. Let $\psi^\varepsilon(t)$ be solution of the Schrödinger equation (1) for a sequence of initial data $(\psi^\varepsilon_0)_{\varepsilon>0}$ with $\Pi^-\psi^\varepsilon_0 = 0$, which is bounded in $L^2(\mathbb{R}^2, \mathbb{C}^2)$, localized in phase space, and which has unique Wigner measures μ_0 and ρ_0 with $\mathrm{supp}(\mu_0) \subset I$. Let

$$C \;:=\; \sup\left\{ \tfrac{1}{2}\,|p|^2 + |q| \;\middle|\; (q,p) \in \mathrm{supp}(\mu_0) \right\}.$$

Then we have for all $t \in [0, T]$

$$\lim_{\varepsilon \to 0} \int_{\{|q|>C\}} |\Pi^+(q)\psi^\varepsilon(t,q)|^2\, dq \;=\; 0\,. \tag{55}$$

Indeed, by Proposition 4 the sequence $(\psi^\varepsilon(t))_{\varepsilon>0}$ is localized in phase space for all $t \in \mathbb{R}$, and we obtain by Proposition 2 that for all $a \in C_b(\mathbb{R}^2, \mathbb{C})$ with $\mathrm{supp}(a) \cap \{q = 0\} = \emptyset$

$$\lim_{\varepsilon \to 0} \int_{\mathbb{R}^2} a(q)\, |\Pi^+(q)\, \psi^\varepsilon(t,q)|^2\, dq \;=\; \int_{\mathbb{R}^4} a(q)\, \mu^+_t(dq, dp)\,,$$

where we have used that that $\mathrm{tr}\big(\Pi^+\psi^\varepsilon(t) \otimes \overline{\psi^\varepsilon}(t)\big) \;=\; |\Pi^+\psi^\varepsilon(t)|^2$ and $\mathrm{tr}(\Pi^+\mu_t) \;=\; \mu^+_t$. Moreover, by the definition of ν^+_t

$$\mu^+_t(q,p) \;=\; \int_{\mathbb{R}} \nu^+_t(q,p,d\eta)\,.$$

By Remark 10, we have $|q^+(t)| \le C$ for all $t \ge 0$, and thus the asserted identity (55).

13 Proof of Theorem 8

With the previous preparations the proof of Theorem 8 is now straightforward.

Proof. We will establish the claimed identity (42) for the Landau-Zener function $W^{\varepsilon}_{LZ}(t)$ in two steps. First, we show that uniformly in $t \in [0,T]$

$$\lim_{\varepsilon\to 0} \int_{\mathbb{R}^4} \operatorname{tr}\left(W^{\varepsilon}(\psi^{\varepsilon}(t))\,(q,p)\,a(q,p)\right) dq\,dp = \int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \operatorname{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right) \quad (56)$$

where the key ingredient is Lemma 14 . Second, we prove

$$\lim_{\varepsilon\to 0} \int_{\mathbb{R}^4} \operatorname{tr}\left(W^{\varepsilon}_{LZ}(t)\,(q,p)\,a(q,p)\right) dq\,dp = \int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \operatorname{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right) \quad (57)$$

uniformly in $t \in [0,T]$, which basically holds by construction of the semigroups.

First Step. We write the diagonal observables a under consideration again in the form $a = \operatorname{tr}(a\,\Pi^+)\Pi^+ + \operatorname{tr}(a\,\Pi^-)\Pi^- =: a^+\,\Pi^+ + a^-\Pi^-$. Note that such observables can be viewed as η-independent elements of $\mathcal{A}$. By Proposition 7, there exists a subsequence $(\varepsilon_k)_{k\in\mathbb{N}}$ depending on $T > 0$ such that

$$\lim_{k\to\infty} \langle W_2^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\rangle_{\mathcal{A}',\mathcal{A}}$$

exists uniformly in $t \in [0,T]$. In the following, we will show that all such convergent subsequences of

$$\left(\langle W_2^{\varepsilon}(\psi^{\varepsilon}(t)), a\rangle_{\mathcal{A}',\mathcal{A}}\right)_{\varepsilon>0} \quad (58)$$

converge to the same limit point

$$\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \operatorname{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right)$$

uniformly in t, and thus the whole sequence itself has to converge towards this limit point uniformly in t. By the definition of the measures $\mu_t^{\pm}$ and $\nu_t^{\pm}$, we have uniformly in t

$$\begin{aligned}\lim_{k\to\infty} \int_{\mathbb{R}^4} \operatorname{tr}\left(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t))\,a(q,p)\right) dq\,dp \;&=\; \lim_{k\to\infty} \langle W_2^{\varepsilon_k}(\psi^{\varepsilon_k}(t)), a\rangle_{\mathcal{A}',\mathcal{A}} \\ &= \sum_{j\in\{\pm\}} \left(\int_{\mathbb{R}^4\setminus I} a^j(q,p)\,\mu_t^j(dq,dp) \;+\; \int_{I\times\overline{\mathbb{R}}} a^j(q,p)\,\nu_t^j(dq,dp,d\eta) \right).\end{aligned}$$

By the identity (51) following Proposition 7

$$\int_{\mathbb{R}^4\setminus I} a^{\pm}(q,p)\,\mu_t^{\pm}(dq,dp) \;=\; \int_{\mathbb{R}^4\setminus I} \left(a^{\pm}\circ\Phi_{\pm}^{-t}\right)(q,p)\,\mu_0^{\pm}(dq,dp)\,.$$

Since the initial data $(\psi_0^{\varepsilon})_{\varepsilon>0}$ have negligible mass near the jump manifold S, that is $\int_{S_\delta} |W^{\varepsilon}(\psi_0^{\varepsilon})(q,p)|\,dq\,dp \to 0$ as $\varepsilon \to 0$, we also have $\int_{\mathbb{R}^4} W^{\varepsilon}(\psi_0^{\varepsilon})(q,p)\,a(q,p)\,dq\,dp \to 0$ as $\varepsilon \to 0$ for all $a \in \mathcal{S}(\mathbb{R}^4, \mathcal{L}(\mathbb{C}^2))$ with $\operatorname{supp}(a) \subset S_\delta$. This means $\operatorname{supp}(\mu_0) \cap S_\delta = \emptyset$, which in turn implies $\mathrm{supp}(\rho_0) \cap (S_\delta \times \overline{\mathbb{R}}) = \emptyset$. By Lemma 14, we then have for the two-scale measures $\nu_t^\pm$

$$\int_{I\times\overline{\mathbb{R}}} a^\pm(q,p)\,\nu_t^+(dq,dp,d\eta) \;=\; \int_{I\times\overline{\mathbb{R}}} \left(\mathcal{T}_\pm^t a\right)(q,p,\eta)\,\nu_0^+(dq,dp,d\eta)\,.$$

Thus, uniformly in t

$$\lim_{k\to\infty} \int_{\mathbb{R}^4} \mathrm{tr}\left(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t))\,a(q,p)\right)\,dq\,dp \;=\;$$
$$\sum_{j\in\{\pm\}} \left(\int_{\mathbb{R}^4\setminus I} \left(a^j \circ \Phi_j^{-t}\right)(q,p)\,\mu_0^j(dq,dp) \;+\; \int_{I\times\overline{\mathbb{R}}} \left(\mathcal{T}_j^t a\right)(q,p,\eta)\,\nu_0^j(dq,dp,d\eta) \right)\,,$$

and by definition of the measure ρ_0 and the semigroup $\mathcal{T}^t$

$$\sum_{j\in\{\pm\}} \int_{I\times\overline{\mathbb{R}}} \left(\mathcal{T}_j^t a\right)(q,p,\eta)\,\nu_0^j(dq,dp,d\eta) \;=\;$$
$$\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\left(\left(\mathcal{T}^t a\right)(q,p)\,\rho_0(dq,dp,d\eta)\right) \;-\; \sum_{j\in\{\pm\}} \int_{\mathbb{R}^4\setminus I} \left(\mathcal{T}_j^t a\right)(q,p,\infty)\,\mu_0^j(dq,dp)\,.$$

Since $T(q,p,\infty) = 0$, we have

$$\int_{\mathbb{R}^4\setminus I} \left(\mathcal{T}_\pm^t a\right)(q,p,\infty)\,\mu_0^\pm(dq,dp) \;=\; \int_{\mathbb{R}^4\setminus I} \left(a^\pm \circ \Phi_\pm^{-t}\right)(q,p)\,\mu_0^\pm(dq,dp)\,,$$

and therefore, uniformly in t,

$$\lim_{k\to\infty} \int_{\mathbb{R}^4} \mathrm{tr}\left(W^{\varepsilon_k}(\psi^{\varepsilon_k}(t))\,a(q,p)\right)\,dq\,dp \;=\; \int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right)\,.$$

The preceding arguments show that all convergent subsequences of the bounded sequence in (58) converge to the same limit, and thus the sequence has to converge itself. This proves (56).

Second Step. In order to establish (57), i.e. to lift the semigroup acting on the measures to a semigroup acting on functionals, we first have to remove a neighborhood of S. Let $\chi \in C^\infty(\mathbb{R},\mathbb{R})$ be a smooth function such that $\chi = 0$ on $[-\delta/2,\delta/2]$ and $\chi = 1$ on $\mathbb{R}\setminus[-\delta,\delta]$. Since $\mathrm{supp}(\rho_0) \cap (S_\delta \times \overline{\mathbb{R}}) = \emptyset$, we have

$$\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right) \;=\; \int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\left(\chi(q\cdot p)\left(\mathcal{T}^t a\right)(q,p,\eta)\,\rho_0(dq,dp,d\eta)\right)\,.$$

Denoting $\widetilde{\chi}(q,p) := \chi(q\cdot p)$, the set $\{\widetilde{\chi}\,(\mathcal{T}^t a) \mid t \in [0,T]\}$ is a bounded subset of $\mathcal{A}$. Since weak*-convergence and strong convergence in $\mathcal{A}'$ coincide, we get uniformly in t

$$\int_{\mathbb{R}^4\times\overline{\mathbb{R}}} \mathrm{tr}\left(a(q,p)\left(\mathcal{T}^t\rho_0\right)(dq,dp,d\eta)\right) \;=\; \lim_{\varepsilon\to 0}\,\left\langle W_2^\varepsilon(\psi_0^\varepsilon), \widetilde{\chi}\left(\mathcal{T}^t a\right)\right\rangle_{\mathcal{A}',\mathcal{A}}\,.$$

Since the initial data have no mass near the jump manifold S, we find that

$$\begin{aligned}
\left\langle W_2^\varepsilon(\psi_0^\varepsilon), \widetilde{\chi}\left(\mathcal{T}^t a\right)\right\rangle_{\mathcal{A}',\mathcal{A}} &= \int_{\mathbb{R}^4} \mathrm{tr}\left(W^\varepsilon(\psi_0^\varepsilon)(q,p)\,\chi(q\cdot p)\,(\mathcal{L}_\varepsilon^t a)(q,p)\right)\,dq\,dp \\
&= \lim_{\varepsilon\to 0}\int_{\mathbb{R}^4} \mathrm{tr}\left(W^\varepsilon(\psi_0^\varepsilon)(q,p)\,(\mathcal{L}_\varepsilon^t a)(q,p)\right)\,dq\,dp \\
&= \lim_{\varepsilon\to 0}\int_{\mathbb{R}^4} \mathrm{tr}\left(W_{\mathrm{LZ}}^\varepsilon(t)(q,p)\,a(q,p)\right)\,dq\,dp\,,
\end{aligned}$$

uniformly in t. This shows (57) and the proof is complete. □

Remark 18 General codimension two crossings with Hamiltonian

$$-\tfrac{\varepsilon^2}{2}\Delta_q + \begin{pmatrix} \alpha(q) & \beta(q) \\ \beta(q) & -\alpha(q) \end{pmatrix},$$

where $\alpha, \beta \in C_b^\infty(\mathbb{R}^n, \mathbb{R})$ are smooth functions with

$$\mathrm{codim}_{\mathbb{R}^n}\{q \in \mathbb{R}^n \mid \alpha(q) = \beta(q) = 0\} = 2\,,$$

lack in their corresponding classical dynamics a second conserved quantity like the angular momentum in the case of the linear conical crossing. Hence, in the general case the τ-dependance of the function ω defining the involutive manifold I_{FG} in (54) cannot be removed, and there seems to be no straightforward way of lifting the Landau-Zener formula for two-scale measures to the level of the Wigner function. ◇

14 Rigorous Surface Hopping Algorithm

The semigroup $\mathcal{L}_\varepsilon^t$ and the Landau-Zener function $W_{\mathrm{LZ}}^\varepsilon(t)$ give rise to the following algorithm to approximate the Wigner function $W^\varepsilon(\psi^\varepsilon(t))$ of the solution $\psi^\varepsilon(t)$ of the model system (1). We assume initial data of the form

$$\psi_0^\varepsilon(q) = \psi_{0,+}^\varepsilon(q)\,\chi^+(q)\,, \qquad q \in \mathbb{R}^2\,,$$

with arbitrary scalar wave function $\psi_{0,+}^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C})$, which is the situation described by Theorem 8. All the trajectories, which occur on the lower level, have been issued by a trajectory of the upper level and move away from the crossing $\{q = 0\}$. There are no leading order interferences between upper and lower electronic level. The final weights $w_j^\pm(T)$, which are produced by the rigorous surface hopping algorithm in Figure 8, are an approximation to the values of the diagonal components $w_\pm^\varepsilon(T)$ of the Wigner function $W^\varepsilon(\psi^\varepsilon(T))$ at the points $(q_j^\pm(T), p_j^\pm(T))$. The number N^- of points on the lower level depends on the initial sample size N^+ and the length of the time interval $[0,T]$. Hence, for computations on large time intervals one might decide not to open up a trajectory for the lower level, if its starting weight

$$|\, T^\varepsilon(q_*, p_*)\, w_j^+(t_*^<)\, | \le \mathrm{tol}$$

Rigorous Surface Hopping Algorithm

1. Compute the Wigner function $W^\varepsilon(\psi^\varepsilon_{0,+}) =: w^\varepsilon_+(0)$ of the initial component $\psi^\varepsilon_{0,+}$. Sample the support of $w^\varepsilon_+(0)$ and call the resulting set

$$\Sigma^+ \;:=\; \big\{(q^+_j, p^+_j) \mid j = 1, \dots, N^+\big\}\,.$$

   With every point $(q^+_j, p^+_j) \in \Sigma^+$ associate the weight $w^+_j(0) := w^\varepsilon_+(0)(q^+_j, p^+_j)$.

2. For all $(q^+_j, p^+_j) \in \Sigma^+$ compute the classical flow $\Phi^t_+(q_j, p_j)$.

3. Denote the point of time and point in phase space, when $\Phi^t_+(q^+_j, p^+_j)$ attains its minimal distance to the crossing $\{q = 0\}$ for the first time, by t_* and (q_*, p_*), respectively. Change the weight

$$w^+_j(0) \;=\; w^+_j(t^<_*) \;\curvearrowright\; w^+_j(t^>_*) \;=\; (1 - T^\varepsilon(q_*, p_*))\, w^+_j(t^<_*)$$

   with

$$T^\varepsilon(q_*, p_*) \;=\; \exp\!\big(-\,\pi\,\tfrac{(q_*\wedge p_*)^2}{|p_*|^3}\big)\,.$$

   Start for time $t = t_*$ a trajectory $\Phi^{t-t_*}_-(q_*, p_*)$ on the lower level, and associate with it the weight $T^\varepsilon(q_*, p_*)\, w^+_j(t^<_*)$.

4. Repeat the procedure described in the previous step for all other times t_*, whenever $\Phi^t_+(q^+_j, p^+_j)$ attains its minimal distance to the crossing $\{q = 0\}$.

Output at time $t = T$: Points in phase space $(q^\pm_j(T), p^\pm_j(T)) \in \mathbb{R}^4$;
Weights $w^\pm_j(T) \in \mathbb{R}$ for $j = 1, \dots, N^\pm$.

Figure 8: The surface hopping algorithm resulting from Theorem 8.

is smaller than some predescribed small tolerance tol $\ll 1$. For the comparative plot in Figure 9, the final squared L^2-norms $\|\Pi^\pm\,\psi^\varepsilon(T)\|^2_{L^2(\mathbb{R}^2)}$ have been approximated by the surface hopping algorithm and by a Strang splitting scheme with Fourier differencing, which is discussed in more detail in Part E later on. The initial plus-component $\psi^\varepsilon_{0,+}$ has been chosen as

$$\psi^\varepsilon_{0,+}(q) \;=\; 2^{-1/2}\,(\varepsilon\pi)^{-1/2}\,\exp\big(-\tfrac{1}{2\varepsilon}\,|q - q_0|^2 + \tfrac{i}{\varepsilon}\,p_0\cdot(q - q_0)\big)\,, \qquad q \in \mathbb{R}^2$$

with $q_0 = (8\sqrt{\varepsilon}, 0)$ and $p_0 = (-1, 0)$. The time-interval for the computation has been chosen as $\big[-2\sqrt{\varepsilon}, 2\sqrt{\varepsilon}\big]$. Hence, the set-up is exactly the same as for the computation producing Figure 1 in Part A. The semi-classical parameter ε has been chosen as $\varepsilon = 10^{-k}$ for $k = 1, \dots, 4$. As expected, the smaller the parameter ε the better the performance of the surface hopping algorithm.

In Part A, Section 3.2, we have given some examples illustrating the ubiquity of conical crossings in the chemical physics' literature. Theoretical chemists have designed innumerous approximation schemes, amongst which J. Tully's surface hopping algorithm of the fewest switches "has turned out to be the most popular approach to describe nonadiabatic dynamics at conical intersections", cit. Section IV in the recent review article [StTh] of the chemists G. Stock and M. Thoss. The algorithm stemming from the aymptotic semigroup $\mathcal{L}_\varepsilon^t$ can be viewed as a rigorously derived variant of the fewest switches approach, which itself is a variation of the originally proposed trajectory surface hopping method of J. Tully and R. Preston [TuPr]. Being aware of the delicate discrepancy in chemical and mathematical lingo and intentions, we do not tackle any systematic comparison between algorithms but just rephrase and quote some passages of the paper [Tu], in which the fewest switches approach has been introduced. J. Tully's algorithm assigns as many initial conditions for classical trajectories "as required to obtain statistically significant conclusions", cit. Section IV. A in [Tu]. Then, the classical equations of motion on each energy level are integrated on a time interval, which is "so long as it is sufficiently short that the electronic probabilities change only slightly". Along the way, a switching probability g is calculated by means of an approximation to the Schrödinger equation for the electronic degrees of freedom. If g is larger than some randomly chosen number, then a trajectory switches to the other energy level and "a velocity adjustment must be made in order to conserve total energy."

In summary, we mention the two key properties, which seem to be shared by all surface hopping type approaches. First, all such algorithms are *grid-free* approximation schemes, an indispensible prerequisite for numerical simulations in molecular dynamics, which are notoriously associated with a high number of degrees of freedom. (Grid-based discretizations scale exponentially in the number of space dimensions.) Second, the numerical integration of *classical transport* equations is by far a much more simpler task than the integration of a highly oscillatory wave function, which pays especially in the physically relevant regime, where the parameter ε ranges from 10^{-3} to 10^{-2}.

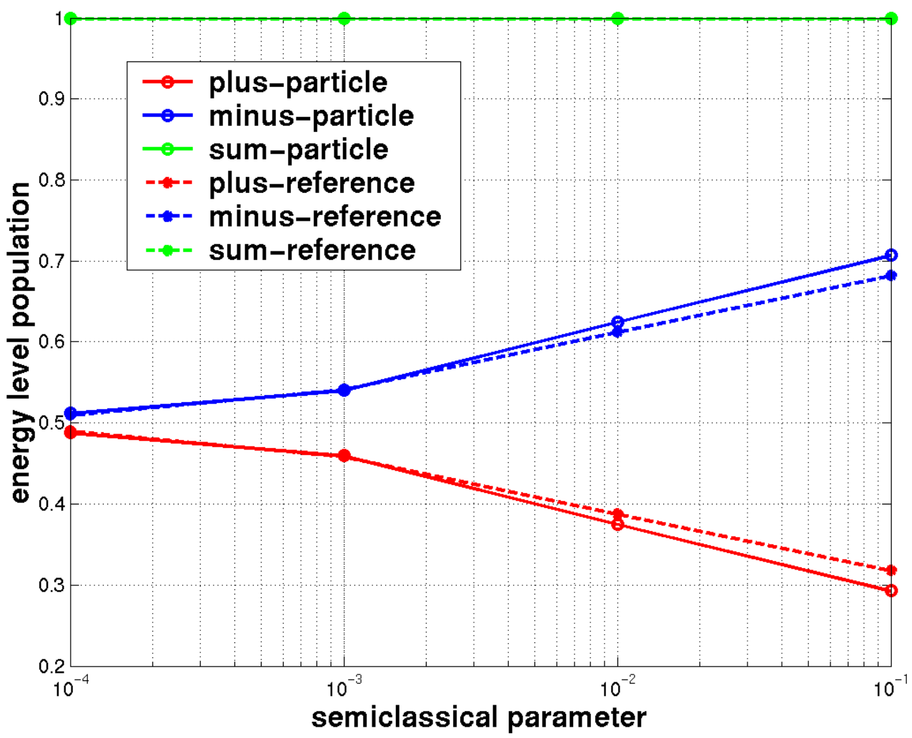


Figure 9: The plot compares the final energy level populations computed by the surface hopping algorithm (particle method, straight lines) and a Strang splitting scheme ("reference solver", dashed lines). Here, by final energy level population the squared L^2-norm $\|\Pi^{\pm}\psi^{\varepsilon}(T)\|^2$ at time $t = T$ is meant. It is plotted against different values of the semiclassical parameter ε, which takes the values $\varepsilon = 10^{-k}$, $k = 1, \dots, 4$. Red lines refer to the upper, blue ones to the lower electronic level. The sum of upper and lower population is plotted in green. The initial data, computational domain and time-interval are exactly the same as for the plots in Figure 1 of Part A. They scale with the parameter ε. The plot affirms our expectations: the smaller the parameter ε the better the performance of the surface hopping algorithm.

Part D

Spectral Study

In this part, we prove that the closure of the model Hamiltonian

$$H^\varepsilon = -\tfrac{\varepsilon^2}{2}\Delta_q + \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}$$

equipped with the domain $D(H^\varepsilon) = C_c^\infty(\mathbb{R}^2, \mathbb{C}^2)$ is of absolutely continuous spectrum, which covers the whole real line,

$$\sigma\big(\overline{H^\varepsilon}\big) = \sigma_{ac}\big(\overline{H^\varepsilon}\big) = \mathbb{R},$$

see Theorem 10 later on. The proof relies on an orbital decomposition, an exact WKB construction, and employs the non-subordinacy method of D. Gilbert and D. B. Pearson for ordinary differential operators.

15 A Direct Sum of Avoided Crossings

Studying resonances associated with conical intersections, L. Nédélec has transformed our system to a direct sum of avoided crossings (see Remark 5.2 in [Ne]). We provide a quick review of this transformation.

First step. We perform a normalized ε-Fourier transformation with respect to $q \in \mathbb{R}^2$,

$$\mathcal{F}_\varepsilon : \psi(q) \mapsto = (2\pi\varepsilon)^{-1} \int_{\mathbb{R}^2} e^{-iq\cdot p/\varepsilon}\, \psi(q)\, dq,$$

which is unitary from $L^2(\mathbb{R}^2, \mathbb{C}^2)$ into itself by Plancherel's Theorem. The original partial differential expression

$$\tau^\varepsilon = -\tfrac{\varepsilon^2}{2}\Delta_q + \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix},$$

becomes

$$\tau_1^\varepsilon = \mathcal{F}^\varepsilon\, \tau^\varepsilon\, (\mathcal{F}^\varepsilon)^{-1} = \tfrac{1}{2}|p|^2 + \begin{pmatrix} -i\varepsilon\partial_{p_1} & -i\varepsilon\partial_{p_2} \\ -i\varepsilon\partial_{p_2} & i\varepsilon\partial_{p_1} \end{pmatrix}.$$

In the original system, the symbol's eigenvalues $|p|^2/2 \pm |q|$ cross for $q = 0$. In the Fourier transformed system, the eigenvalues are $|q|^2/2 \pm |p|$, and the crossing has moved from position to momentum space onto the set $\{p = 0\}$.

Second step. Using the rotational symmetry of the potential $\frac{1}{2}|p|^2$, we switch to polar coordinates $p = r(\cos\phi, \sin\phi)$, that is we identify

$$L^2(\mathbb{R}^2, \mathbb{C}^2; dp_1\, dp_2) = L^2(\,]0,\infty[\times\mathbb{T}, \mathbb{C}^2; r\, dr\, d\phi) =: \mathcal{L}_{per}(r\, dr\, d\phi).$$

In polar coordinates, we obtain the partial differential expression

$$\tau_2^\varepsilon = \tfrac{1}{2}r^2 - i\varepsilon\partial_r \begin{pmatrix} \cos\phi & \sin\phi \\ \sin\phi & -\cos\phi \end{pmatrix} + \begin{pmatrix} -\sin\phi & \cos\phi \\ \cos\phi & \sin\phi \end{pmatrix} \tfrac{1}{r}\,(-i\varepsilon\partial_\phi).$$

The symbol in polar coordinates has the eigenvalues

$$\tfrac{1}{2}r^2 \pm \sqrt{\rho^2 + \tfrac{\nu^2}{r^2}}, \qquad (r, \phi, \rho, \nu) \in\,]0,\infty[\times\mathbb{T}\times\mathbb{R}^2,$$

which cross for $\rho = \nu = 0$.

Third step. Similarly to Prüfer's transformation of ordinary differential operators, see Chapter 8.3 in [Hi], we conjugate by a unitary operator, which is multiplication by a half-angle rotation matrix. Denoting

$$\mathcal{L}_{\mathrm{sem}}(r\,dr\,d\phi) \;:=\; \{\psi \in L^2(]0,\infty[\times[0,2\pi],\mathbb{C}^2; r\,dr\,d\phi) \mid \psi(\cdot,0) = -\psi(\cdot,2\pi)\}\,,$$

we conjugate by

$$R : \mathcal{L}_{\mathrm{per}}(r\,dr\,d\phi) \to \mathcal{L}_{\mathrm{sem}}(r\,dr\,d\phi)\,, \qquad \psi(r,\phi) \mapsto \begin{pmatrix} \cos\frac{\phi}{2} & \sin\frac{\phi}{2} \\ -\sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix} \psi(r,\phi)\,.$$

We note, that R takes functions, which are periodic in the angular variable, to semi-periodic ones. That way, we obtain the partial differential expression

$$\tau_3^\varepsilon \;=\; \tfrac{1}{2}r^2 + \begin{pmatrix} -i\varepsilon\partial_r & -r^{-1}\,i\varepsilon\partial_\phi \\ -r^{-1}\,i\varepsilon\partial_\phi & i\varepsilon\partial_r \end{pmatrix} - \tfrac{i\varepsilon}{2r}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Remark 19 At this point we note, that the the Weyl quantization of the tempered distributions $\sigma_1(q,p) = |p|^{-1}(q\cdot p)$ and $\sigma_2(q,p) = |p|^{-1}(q \wedge p)$ reads in Fourier transformed polar coordinates as

$$\sigma_1(q,-i\varepsilon\nabla_q) \;\simeq\; -i\varepsilon\partial_r - i\varepsilon\,\tfrac{1}{2r}\,, \qquad \sigma_2(q,-i\varepsilon\nabla_q) \;\simeq\; -i\varepsilon\,\tfrac{1}{r}\,\partial_\phi\,.$$

Hence, the derivation of τ_3^ε has justified the unitary equivalence, which had been claimed in Section 10 of Part C. ♢

Fourth Step. To remove the subprincipal part, we conjugate by the operator multiplying with $r^{-1/2}$. For this, we set

$$\mathcal{L}_{\mathrm{sem}}(dr\,d\phi) \;:=\; \{\psi \in L^2(]0,\infty[\times[0,2\pi],\mathbb{C}^2; dr\,d\phi) \mid \psi(\cdot,0) = -\psi(\cdot,2\pi)\}$$

and

$$S : \mathcal{L}_{\mathrm{sem}}(r\,dr\,d\phi) \;\to\; \mathcal{L}_{\mathrm{sem}}(dr\,d\phi)\,, \qquad \psi(r,\phi) \mapsto r^{-1/2}\,\psi(r,\phi)\,.$$

This unitary transformation results in the partial differential expression

$$\tau_4^\varepsilon \;=\; \tfrac{1}{2}r^2 + \begin{pmatrix} -i\varepsilon\partial_r & -r^{-1}\,i\varepsilon\partial_\phi \\ -r^{-1}\,i\varepsilon\partial_\phi & i\varepsilon\partial_r \end{pmatrix}.$$

Summarizing the preceding steps, there is a unitary mapping

$$U_4^\varepsilon :\; L^2(\mathbb{R}^2,\mathbb{C}^2; dp_1\,dp_2) \to \mathcal{L}_{\mathrm{sem}}(dr\,d\phi)\,, \qquad U_4^\varepsilon \;=\; S\circ R\circ \mathcal{F}_\varepsilon$$

such that

$$U_4\,\tau^\varepsilon\,U_4^* \;=\; \tau_4^\varepsilon\,.$$

Fifth Step. An ε-scaled Fourier series expansion with respect to the semi-periodic angular variable ϕ gives the decomposition

$$\tau_4^\varepsilon \;=\; \bigoplus_{\nu\in\,\varepsilon(\mathbb{Z}+1/2)} \tfrac{1}{2}r^2 + \begin{pmatrix} -i\varepsilon\partial_r & \frac{\nu}{r} \\ \frac{\nu}{r} & i\varepsilon\partial_r \end{pmatrix} \;=:\; \bigoplus_{\nu\in\,\varepsilon(\mathbb{Z}+1/2)} \tau_\nu^\varepsilon\,.$$

The ordinary differential expressions τ_ν^ε with $\nu \in \varepsilon(\mathbb{Z}+1/2)$ operate in $L^2(]0,\infty[,\mathbb{C}^2;dr)$. They are of the form

$$\tau_\nu^\varepsilon\, u(r) \;=\; p_\nu(r)\, u(r) + (q - q^*)\, \partial_r u(r)$$

with

$$p_\nu(r) \;=\; \begin{pmatrix} \frac{1}{2}\,r^2 & \frac{\nu}{r} \\ \frac{\nu}{r} & \frac{1}{2}\,r^2 \end{pmatrix} \qquad \text{and} \qquad q \;=\; -\tfrac{1}{2}\,i\varepsilon \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{59}$$

and thus fall into the class of formally self-adjoint differential expressions as defined in Chapter 1 of [We87]. The eigenvalues of the symbol of τ_ν^ε are those of τ_2^ε. However, since $\nu \in \varepsilon(\mathbb{Z}+1/2)$ is now of the form ε times an integer plus one half, the conical crossing has turned into a family of avoided crossings. We note, that a similar orbital decomposition has also been given by J. Avron and A. Gordon in [AvGo]. They use their decomposition to construct an approximate solution of the zero-energy problem $\tau^\varepsilon\, u \,=\, 0$ in terms of generalized hypergeometric functions.

16 Exact WKB Solutions

For a spectral analysis of the self-adjoint realization of the differential expressions τ_ν^ε in $L^2(]0,\infty[,\mathbb{C}^2;dr)$ we construct exact WKB solutions of the ordinary differential equations $(\tau_\nu^\varepsilon - \lambda)\, u = 0$ with $\lambda \in \mathbb{C}$. Since it does not cost any extra effort, we construct solutions for differential equations of the slightly more general form

$$p(x)\, u(x) + (q - q^*)\, \partial_x u(x) \;=\; 0\,, \qquad x \in I \subset \mathbb{R} \tag{60}$$

with

$$p(x) \;=\; \begin{pmatrix} p_1(x) & \omega(x) \\ \omega(x) & p_2(x) \end{pmatrix}, \qquad z \in \mathcal{S}\,,$$

such that $p_1, p_2 : \mathcal{S} \to \mathbb{C}$ and $\omega : \mathcal{S} \to \mathbb{R}$ are analytic functions, $\mathcal{S} \subset \mathbb{C}$ a strip in the complex plane containing the interval $I \subset \mathbb{R}$ the solutions shall live on, and

$$q \;=\; -\tfrac{1}{2}\,i\varepsilon \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

We start by the formal construction, postponing any rigorous considerations to the next but one section.

16.1 Formal Construction

After conjugation by

$$N(x) := \tfrac{1}{2}\,\exp\left(\tfrac{i}{2\varepsilon}\int_0^x (p_{11}(y) - p_{22}(y))\,dy\right)\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} =: \tfrac{1}{2}\,n(x)\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$$

system (60) is transformed into the trace-free system

$$i\varepsilon\,\partial_x v(x) \;=\; \begin{pmatrix} 0 & \tfrac{1}{2}(p_1(x)+p_2(x)) + \omega(x) \\ \tfrac{1}{2}(p_1(x)+p_2(x)) - \omega(x) & 0 \end{pmatrix} v(x)$$

with $v(x) = N(x)u(x)$. Introducing new, complex coordinates

$$z(x) = \int_{x_0}^{x} \sqrt{-\tfrac{1}{4}(p_1(y)+p_2(y))^2 + \omega(y)^2}\,dy\,, \qquad x_0 \in \mathcal{S}\,, \tag{61}$$

we look for solutions of the form $v(x) = e^{\pm z(x)/\varepsilon}\,\widetilde{w}_\pm(z(x))$.

Definition 13 (Turning Point) Let $p_1, p_2 : \mathcal{S} \to \mathbb{C}$ and $\omega : \mathcal{S} \to \mathbb{R}$ be analytic functions on some strip $\mathcal{S} \subset \mathbb{C}$ containing some interval $I \subset \mathbb{R}$. The zeros of the function

$$\mathcal{S} \to \mathbb{C}\,, \qquad x \mapsto -\tfrac{1}{4}(p_1(x)+p_2(x))^2 + \omega^2(x)$$

are called the *turning points* of the system (60).

We note, that due to the possible presence of such turning points the square root in the definition of $z(x)$ might be defined only *locally*. By formal calculations, the amplitude vector $\widetilde{w}_\pm(z)$ has to satisfy

$$-i\varepsilon\,\partial_z \widetilde{w}_\pm(z) = \begin{pmatrix} \pm i & H(z) \\ -H(z)^{-1} & \pm i \end{pmatrix} \widetilde{w}_\pm(z)\,,$$

where the function $H(z(x))$ is given by

$$\begin{aligned} H(z(x)) \;&=\; \left(\tfrac{1}{2}(p_1(x)+p_2(x)) + \omega(x)\right)\left(-\tfrac{1}{4}(p_1(x)+p_2(x))^2 + \omega(x)^2\right)^{-1/2} \\ &=\; -i\,\mathrm{sgn}\left(\tfrac{1}{2}(p_1(x)+p_2(x)) + \omega(x)\right)\sqrt{\frac{\tfrac{1}{2}(p_1(x)+p_2(x)) + \omega(x)}{\tfrac{1}{2}(p_1(x)+p_2(x)) - \omega(x)}}\,. \end{aligned}$$

The turning points are the poles and zeros of the meromorphic function $x \mapsto H(z(x))$. For a decomposition with respect to image and kernel of the preceding system's matrix we formally conjugate by

$$P_\pm(z) \;=\; 2^{-\frac{1}{2}}\begin{pmatrix} H(z)^{-\frac{1}{2}} & \pm i\,H(z)^{\frac{1}{2}} \\ H(z)^{-\frac{1}{2}} & \mp i\,H(z)^{\frac{1}{2}} \end{pmatrix}$$

and obtain a system for $w_\pm(z) = P_\pm(z)\widetilde{w}_\pm(z)$,

$$\partial_z w_\pm(z) = \begin{pmatrix} 0 & -\frac{H'(z)}{2H(z)} \\ -\frac{H'(z)}{2H(z)} & \mp 2/\varepsilon \end{pmatrix} w_\pm(z)\,,$$

where $H'(z)$ is shorthand for $\partial_z H(z)$. The series ansatz

$$w_\pm(z) = \sum_{n\geq 0} \begin{pmatrix} w_{2n,\pm}(z) \\ w_{2n+1,\pm}(z) \end{pmatrix} \tag{62}$$

with $w_{0,\pm} \equiv 1$ and

$$\begin{aligned} \left(\partial_z \pm \tfrac{2}{\varepsilon}\right) w_{2n+1,\pm}(z) &= -\frac{H'(z)}{2H(z)}\, w_{2n,\pm}(z)\,, \\ \partial_z w_{2n+2,\pm}(z) &= -\frac{H'(z)}{2H(z)}\, w_{2n+1,\pm}(z)\,, \quad n \geq 0\,, \end{aligned}$$

gives us a formal solution, which is unique up to some arbitrary constants. The constants are fixed by setting

$$w_{n,\pm}(\widetilde{z}) = 0\,, \quad n \geq 1$$

for some suitable base point $\widetilde{z} \in \mathcal{S}$. We note, that the preceding equations for $w_{n,\pm}$ are the same as the ones obtained by an exact WKB construction for scalar Schrödinger equations, see for example the work of C. Gerard and A. Grigis [GeGr] or T. Ramond [Ra]. If $\Gamma_\pm(\widetilde{z}, z)$ denotes a path of finite length in $\mathcal{S}$ connecting $\widetilde{z}$ and $z \in \mathcal{S}$, we can formally rewrite the above differential equations for $n \geq 0$ as

$$\begin{aligned} w_{2n+1,\pm}(z) &= -\int_{\Gamma_\pm(\widetilde{z},z)} \exp\left(\pm \tfrac{2}{\varepsilon}(\zeta - z)\right) \frac{H'(\zeta)}{2H(\zeta)}\, w_{2n,\pm}(\zeta)\, d\zeta, \\ w_{2n+2,\pm}(z) &= -\int_{\Gamma_\pm(\widetilde{z},z)} \frac{H'(\zeta)}{2H(\zeta)}\, w_{2n+1,\pm}(\zeta)\, d\zeta \end{aligned}$$

or after iterated integration as

$$\begin{aligned} w_{2n+1,\pm}(z) &= -\int_{\Gamma_\pm(\widetilde{z},z)} \int_{\Gamma_\pm(\widetilde{z},\zeta_{2n+1})} \cdots \int_{\Gamma_\pm(\widetilde{z},\zeta_1)} \exp\left(\pm \tfrac{2}{\varepsilon}(\zeta_2 - \zeta_3 + \ldots + \zeta_{2n+1} - z)\right) \times \\ &\qquad \times \frac{H'(\zeta_1)}{2H(\zeta_1)} \cdots \frac{H'(\zeta_{2n+1})}{2H(\zeta_{2n+1})}\, d\zeta_1 \ldots d\zeta_{2n+1}\,, \end{aligned}$$

$$\begin{aligned} w_{2n+2,\pm}(z) &= -\int_{\Gamma_\pm(\widetilde{z},z)} \int_{\Gamma_\pm(\widetilde{z},\zeta_{2n+2})} \cdots \int_{\Gamma_\pm(\widetilde{z},\zeta_1)} \exp\left(\pm \tfrac{2}{\varepsilon}(\zeta_2 - \zeta_3 + \ldots - \zeta_{2n+2})\right) \times \\ &\qquad \times \frac{H'(\zeta_1)}{2H(\zeta_1)} \cdots \frac{H'(\zeta_{2n+2})}{2H(\zeta_{2n+2})}\, d\zeta_1 \ldots d\zeta_{2n+2}\,. \end{aligned}$$

16.2 Convergence

Now, we should give the preceding formal construction some mathematical meaning on open, simply connected domains $\Omega \subset \mathcal{S}$, which do *not* contain any turning points. On such domains Ω, all the functions defined above are well-defined analytic functions. For compact subsets $K \subset \Omega$ and $\widetilde{z}, z \in z(K)$ there exist positive constants $C^\varepsilon_\pm(K) > 0$ depending on the semi-classical parameter ε and the compactum K such that

$$\sup_{\zeta \in \Gamma_\pm(\widetilde{z},z)} \left| \exp\left(\pm \tfrac{2}{\varepsilon}\zeta\right) \frac{H'(\zeta)}{2H(\zeta)} \right| \;\leq\; C^\varepsilon_\pm(K)\,.$$

If we denote the maximal length of the pathes $\Gamma_\pm(\widetilde{z},\cdot) \subset K$ in the preceding iterated integrations by $0 < L < \infty$, then

$$\sup_{z\in z(K)} |w_{n,\pm}(z)| \;\leq\; \frac{C^{\varepsilon}_{\pm}(K)^n\, L^n}{n!}\,, \qquad n \geq 0\,,$$

where the bound $\frac{L^n}{n!}$ comes from the volume of a simplex with length L. Thus, we have uniform convergence of the series (62) for $w_\pm(z)$ and exact solutions

$$u_\pm(x) \;=\; e^{\pm\, z(x)/\varepsilon}\, n(x)^{-1}\, T_\pm(z(x))\, w_\pm(z(x))$$

of the original problem (60) on turning point free compact sets K, where

$$T_\pm(z) \;=\; 2^{-\frac{1}{2}} \begin{pmatrix} H(z)^{\frac{1}{2}} \mp iH(z)^{-\frac{1}{2}} & H(z)^{\frac{1}{2}} \pm iH(z)^{-\frac{1}{2}} \\ -H(z)^{\frac{1}{2}} \mp iH(z)^{-\frac{1}{2}} & -H(z)^{\frac{1}{2}} \pm iH(z)^{-\frac{1}{2}} \end{pmatrix}, \qquad z \in z(K)\,.$$

16.3 Original Equations

Now we turn to back to the linear conical crossing problem, for which we want to study solutions of the systems

$$(\tau^{\varepsilon}_{\nu} - \lambda)\, u(r) \;=\; \begin{pmatrix} \frac{1}{2}r^2 - \lambda - i\varepsilon\partial_r & \frac{\nu}{r} \\ \frac{\nu}{r} & \frac{1}{2}r^2 - \lambda + i\varepsilon\partial_r \end{pmatrix} u(r) \;=\; 0\,, \qquad r \in]0,\infty[\,,$$

for $\lambda \in \mathbb{C}$ and $\nu \in \varepsilon(\mathbb{Z}+1/2)$. Following the preceding construction, we obtain for some suitable $r_0 \in \mathbb{C}^+$ the phase function

$$z(r, r_0) = \int_{r_0}^{r} \sqrt{-(\tfrac{1}{2}s^2 - \lambda)^2 + (\tfrac{\nu}{s})^2}\; ds\,.$$

The turning points are the roots of the two cubic polynomials $r^3 - 2\lambda r \pm 2|\nu|$, which lie in the right half-plane. Solving the cubic equations by Cardano's method, we obtain six complex roots of the form

$$u^\pm + v^\pm\,, \qquad -\tfrac{1}{2}(u^\pm + v^\pm) \pm \tfrac{i}{2}\sqrt{3}\,(u^\pm - v^\pm)$$

with $u^\pm = (\mp|\nu| + \sqrt{D}\,)^{1/3}$, $v^\pm = 2\lambda/(3u^\pm)$, and determinant $D = (-2\lambda/3)^3 + \nu^2$. Depending on the determinant D, we have two different cases. For $D = 0$, we have a simple root $2\,|\nu|^{1/3}$ and a double root $|\nu|^{1/3}$. For $D \neq 0$, we have three distinct roots in the right half-plane, one close to zero and the other two close to $\sqrt{2|\lambda|}$. The function H is

$$H(z(r)) \;=\; -i\,\mathrm{sgn}(\,\tfrac{1}{2}r^3 - \lambda r + \nu\,)\sqrt{\left(\tfrac{1}{2}r^3 - \lambda r + \nu\right)\left(\tfrac{1}{2}r^3 - \lambda r - \nu\right)^{-1}}\,.$$

17 Spectrum of the Differential Operators

The original partial differential expression τ^{ε} in $L^2(\mathbb{R}^2, \mathbb{C}^2; dq_1\, dq_2)$ is unitarily equivalent to the direct sum of ordinary differential expressions τ^{ε}_{ν} in $L^2(]0,\infty[, \mathbb{C}^2; dr)$. For the following considerations, we fix $\varepsilon > 0$ and $\nu \in \varepsilon(\mathbb{Z}+1/2)$ to study the spectrum of the self-adjoint realization of τ^{ε}_{ν} in $L^2(]0,\infty[, \mathbb{C}^2; dr)$.

17.1 Essential Spectrum

We obtain all self-adjoint realizations in $L^2(]0,\infty[,\mathbb{C}^2;dr)$ as restrictions of the maximal operator M^ε_ν

$$D(M^\varepsilon_\nu) \;=\; \{\,u \in AC(]0,\infty[,\mathbb{C}^2) \mid \tau^\varepsilon_\nu\, u \in L^2(]0,\infty[,\mathbb{C}^2;dr)\,\}\,, \quad M^\varepsilon_\nu\, u \;=\; \tau^\varepsilon_\nu\, u\,,$$

where $AC(]0,\infty[,\mathbb{C}^2)$ denotes the space of absolutely continuous functions. The maximal operator M^ε_ν is densely defined and closed, see Theorem 3.9 in [We87]. Existence of self-adjoint restrictions is guaranteed, if the deficiency indices

$$\gamma_\pm \;:=\; \dim\ker(\mp i - M^\varepsilon_\nu)$$

are equal. For the computation of these indices we use the asymptotics of the exact WKB solutions $u_\pm$ of $(\tau^\varepsilon_\nu - \lambda)\,u = 0$ with $\lambda \in \mathbb{C}$ for $r \to 0$ and $r \to \infty$. The following lemma's proof relies on a decomposition method given in Theorem 4.2 in [We87].

Lemma 15 (Deficiency Indices) *Let $\varepsilon > 0$ and $\nu \in \varepsilon(\mathbb{Z}+1/2)$. The deficiency indices $\gamma_\pm$ of the maximal operator M^ε_ν are both equal zero.*

Proof. The space of all solutions of $(\tau^\varepsilon_\nu - \lambda)\,u = 0$ has dimension two. Since $\gamma_\pm = \gamma_0^\pm + \gamma_\infty^\pm - 2$, we have proven our claim, if we show

$$\gamma_\infty^\pm \;=\; \gamma_0^\pm \;=\; 1\,.$$

The indices $\gamma_\infty^\pm$ and $\gamma_0^\pm$ are defined as the number of linearly independent solutions of $(\mp i - \tau^\varepsilon_\nu)\,u = 0$, which lie left respectively right in $L^2(]0,\infty[,\mathbb{C}^2;dr)$. A function lies left respectively right in $L^2(]0,\infty[,\mathbb{C}^2;dr)$, if it is square-integrable on $]0,c[$ respectively $]c,\infty[$ for all $c \in]0,\infty[$. We start with the computation of $\gamma_\infty^\pm$. Clearly, $H(z(r)) \to -i$ as $r \to \infty$. Choosing the amplitude base point $\widetilde{z} = \lim_{r\to\infty} z(r)$, we have $w_\pm(z(r)) \to (1,0)^t$ as $r \to \infty$, and

$$\lim_{r\to\infty}\; T_\pm(H(z(r)))\; w_\pm(z(r)) \;=\; 2^{-1/2}\, e^{-i\pi/4} \begin{pmatrix} -1 \mp 1 \\ 1 \mp 1 \end{pmatrix}.$$

Hence, the decay properties of the exact WKB solutions $u_\pm$ at infinity are governed by the exponential term $e^{\pm z(r)/\varepsilon}$. Let $x \in \mathbb{C}$. Taylor expansion of the function $y \mapsto \sqrt{x+y}$, gives for all $y > 0$ with $y \neq x$ some $\eta \in]0,y[$ such that

$$\sqrt{x+y} \;=\; \sqrt{x} + \tfrac{1}{2}\, y\, (x+\eta)^{-1/2}\,.$$

Setting $x = -\left(\frac{1}{2}\, s^2 - \lambda\right)^2$ with $\lambda \in \{\pm i\}$ and $y = (\nu/s)^2$, we have some $\eta_s \in]0,(\nu/s)^2[$ such that

$$\begin{aligned} \pm\sqrt{-i\left(\tfrac{1}{2}\, s^2 - \lambda\right)^2 \pm \left(\tfrac{\nu}{s}\right)^2} \;&=\; \pm i\left(\tfrac{1}{2}\, s^2 - \lambda\right) + \tfrac{1}{2}\,\left(\tfrac{\nu}{s}\right)^2 \left(-\left(\tfrac{1}{2}\, s^2 - \lambda\right)^2 + \eta_s\right)^{-1/2} \\ &=\; \pm i\left(\tfrac{1}{2}\, s^2 - \lambda\right) + \mathcal{O}(\,s^{-4}\,) \qquad \text{as} \qquad s \to \infty\,. \end{aligned}$$

Hence, there is a constant 'const.' depending on the choice of the phase base point r_0 such that

$$\pm z(r) \;=\; \pm i\,(r^3 - \lambda r) + \text{const.} + \mathcal{O}(r^{-3}) \qquad \text{as} \qquad r \to \infty\,,$$

and we see the proportionality

$$e^{\pm z(r)/\varepsilon} \sim e^{\pm i\,(r^3-\lambda r)/\varepsilon} \qquad \text{as} \qquad r \to \infty\,. \tag{63}$$

Therefore, only one of the solutions $u_\pm$ is square-integrable at infinity, which means that $\gamma_\infty^\pm = 1$. It remains to compute $\gamma_0^\pm$. We have $H(z(0)) = \mathrm{sgn}(\nu)$. Choosing the amplitude base point $\widetilde{z} = z(0)$, we obtain $w_\pm(z(0)) = (1,0)^t$ and hence

$$T_\pm(H(z(0)))\, w_\pm(z(0)) \;=\; 2^{-1/2} \begin{pmatrix} 1 \mp i \\ -1 \mp i \end{pmatrix} \qquad \text{resp.} \qquad 2^{-1/2} \begin{pmatrix} i \mp 1 \\ -i \mp 1 \end{pmatrix},$$

if $\nu > 0$ respectively $\nu < 0$. Thus, we examine the exponential term $e^{\pm z(0)/\varepsilon}$. A Taylor expansion argument similar to the one before gives

$$\pm\sqrt{-\left(\tfrac{1}{2}\,s^2-\lambda\right)^2+\left(\tfrac{\nu}{s}\right)^2} \;=\; \pm\,\tfrac{|\nu|}{s} + \mathcal{O}(s) \qquad \text{as} \qquad s \to 0$$

and

$$\pm\, z(r) \;=\; \pm\,|\nu| \ln r + \text{const.} + \mathcal{O}(r^2) \qquad \text{as} \qquad r \to 0\,,$$

where ‘const.’ depends on the choice of the phase base point r_0. Hence, we have the proportionality

$$e^{\pm z(r)/\varepsilon} \sim r^{\pm|\nu|/\varepsilon} \qquad \text{as} \qquad r \to 0\,. \tag{64}$$

Thus, only one of the exact WKB solutions $u_\pm$ is square-integrable at zero, and we obtain $\gamma_0^\pm = 1$. □

Having deficiency indices $\gamma_\pm$, which are not only equal but identical zero, the maximal operator M_ν^ε is the unique self-adjoint realization of τ_ν^ε in $L^2(]0,\infty[,\mathbb{C}^2;dr)$, see Theorem 4.6 in [We87]. This observation can also be paraphrased, that the minimal operator m_ν^ε,

$$D(m_\nu^\varepsilon) \;=\; C_c^\infty(\,]0,\infty[,\mathbb{C}^2\,)\,, \qquad m_\nu^\varepsilon\, u \;=\; \tau_\nu^\varepsilon\, u\,,$$

is essentially self-adjoint and has as its closure the maximal operator. However, there is more to deduce from the asymptotics of the exact WKB solutions.

PROPOSITION 8 (ESSENTIAL SPECTRUM) *Let $\varepsilon > 0$ and $\nu \in \varepsilon(\mathbb{Z}+1/2)$. The maximal operator M_ν^ε is the unique self-adjoint realization of the differential expression τ_ν^ε in $L^2(]0,\infty[,\mathbb{C}^2;dr)$, and we have*

$$\sigma(M_\nu^\varepsilon) \;=\; \sigma_{\mathrm{ess}}(M_\nu^\varepsilon) \;=\; \mathbb{R}\,.$$

PROOF. We show $\lambda \in \sigma_{\mathrm{ess}}(M_\nu^\varepsilon)$ for all $\lambda \in \mathbb{R}$. We denote by $\gamma_{0,\lambda}$ and $\gamma_{\infty,\lambda}$ the number of linearly independent solutions of $(\tau_\nu^\varepsilon - \lambda)\,u = 0$, which are square-integrable at zero respectively infinity. Equations (64) and (63) imply

$$\gamma_{0,\lambda} + \gamma_{\infty,\lambda} \;=\; 1 + 0 \;<\; 2 + \gamma_\pm \;=\; 2 + 0\,.$$

Hence, by Theorem 11.1 in [We87] we obtain $\lambda \in \sigma_{\mathrm{ess}}(M_\nu^\varepsilon)$. □

Next, we prove absence of singular continuous spectrum, which requires a bit more technique.

17.2 Absolutely Continuous Spectrum

We have read off from equation (63), that at least one of the exact WKB solutions $u_\pm$ of $(\tau_\nu^\varepsilon - \lambda)\, u = 0$ for $\lambda \in \mathbb{C}$ lacks square-integrability at infinity. Thus, we have already proven, that the differential expressions τ_ν^ε are in the limit point case at infinity.

Lemma 16 (Limit Point Case) *The differential expressions τ_ν^ε, $\nu \in \varepsilon(\mathbb{Z}+1/2)$, $\varepsilon > 0$, are in the limit point case at infinity. That is, for every $\lambda \in \mathbb{C}$ there is at least one solution of $(\tau_\nu^\varepsilon - \lambda)\, u = 0$, which is not square-integrable at infinity.*

For real $\lambda \in \mathbb{R}$ the two exact WKB solutions $u_\pm$ lack not only square-integrability at infinity, but they are also of the same size at infinity. Such an asymptotic behaviour enables us to apply the non-subordinacy method of D. Gilbert and D. B. Pearson, which initially has been developed for the spectral study of one-dimensional Schrödinger operators [GiPe]. We will use the uniform non-subordinacy condition proposed in [We96], which will simplify the proofs later on.

Definition 14 (Same Size) Let $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z}+1/2)$, and $I \subset \mathbb{R}$ an interval. If there exist positive $\theta > 0$, $c > 0$, and a function $k :]c,\infty[\to]0,\infty[$ such that all solutions of $(\tau_\nu^\varepsilon - \lambda)\, u = 0$ for $\lambda \in I$ with $|u(c)| = 1$ satisfy

$$\theta\, k(R) \;\le\; \int_c^R |u(r)|^2\, dr \;\le\; k(R) \qquad \text{for all} \quad R > c\,,$$

then all solutions of $(\tau_\nu^\varepsilon - \lambda)\, u = 0$ for $\lambda \in I$ are *of the same size* at infinity.

We note, that if this uniform non-subordinacy condition is satisfied for some constant $c > 0$, then it also holds for all other $c' \in]0,c[$ with different $\theta' > 0$ and $k' :]c',\infty[\to]0,\infty[$.

Lemma 17 (Same Size) *Let $\varepsilon > 0$ and $\nu \in \varepsilon(\mathbb{Z}+1/2)$. For all compact intervals $I \subset \mathbb{R}$, the solutions of $(\tau_\nu^\varepsilon - \lambda)\, u = 0$ for $\lambda \in I$ are of the same size at infinity.*

Proof. We deduce from the proof of Lemma 15 the existence of constants $0 \neq C_\lambda \in \mathbb{C}$ such that the WKB solutions $u_\pm(r) = u_\pm(r;\lambda)$ are equivalent to

$$v_\pm(r;\lambda) \;:=\; C_\lambda\, e^{\pm i (r^3 - \lambda r)/\varepsilon} \begin{pmatrix} 1/2 \pm 1/2 \\ 1/2 \mp 1/2 \end{pmatrix}$$

as $r \to \infty$, where the limit is uniform in $\lambda \in I$. The constants C_λ are bounded away from zero such that $\inf_{\lambda\in I} |C_\lambda| > \delta_1$ for some $\delta_1 > 0$. Let $\delta_2 > 0$ be another small constant such that $\inf_{\lambda\in I}(|C_\lambda| - \delta_1)^2 > \delta_2$. We choose $c > 0$ such that for all $\lambda \in I$ and for all $r \ge c$

$$|\, u_\pm(r;\lambda) - v_\pm(r;\lambda)\,| \le\; \delta_1 \qquad \text{and} \qquad |\, \langle u_+(r;\lambda), u_-(r;\lambda)\rangle \,| \le\; \delta_2\,.$$

For every solution $u(r) = u(r;\lambda)$ with $|u(c;\lambda)| = 1$ there are $\alpha_\pm(\lambda) \in \mathbb{C}$ such that

$$u(r;\lambda) \;=\; \alpha_+(\lambda)\, u_+(r;\lambda) + \alpha_-(\lambda)\, u_-(r;\lambda)\,, \qquad r \in [c,\infty[$$

with $\sup_{\lambda\in I} |\alpha_\pm(\lambda)|^2 \le A < \infty$. Since

$$(R-c)\,(|C_\lambda| - \delta_1)^2 \;\le\; \int_c^R |u_\pm(r;\lambda)|^2\,dr \;\le\; (R-c)\,(|C_\lambda| + \delta_1)^2\,,$$

we obtain

$$(R-c)\,2A\,\left((|C_\lambda| - \delta_1)^2 - \delta_2\right) \;\le\; \int_c^R |u(r;\lambda)|^2\,dr \;\le\; (R-c)\,2A\,\left((|C_\lambda| + \delta_1)^2 + \delta_2\right)\,.$$

□

For Sturm-Liouville and Dirac differential expressions, which are in the limit point case at infinity and have solutions of the same size at infinity, J. Weidmann has proven absolute continuous spectrum for their self-adjoint realizations, see Theorem 3 in [We96]. The same result is true in our case.

THEOREM 9 (ABSOLUTELY CONTINUOUS SPECTRUM) *Let* $\varepsilon > 0$ *and* $\nu \in \varepsilon(\mathbb{Z} + 1/2)$. *We have for the self-adjoint realization* M_ν^ε *on* $L^2(]0,\infty[,\mathbb{C}^2;dr)$ *of the ordinary differential expression* τ_ν^ε

$$\sigma(M_\nu^\varepsilon) \;=\; \sigma_{ac}(M_\nu^\varepsilon) \;=\; \mathbb{R}\,.$$

The proof is analogous to the proof of the corresponding result for Sturm-Liouville and Dirac differential expressions. Before convincing ourselves of this analogy in Section 17.5, we need some information about the self-adjoint realizations of τ_ν^ε on $L^2(]c,R[,\mathbb{C}^2;dr)$ with $c \ge 0$ and $c < R \le \infty$.

17.3 BOUNDARY CONDITIONS

Since the matrix-valued function $r \mapsto p_\nu(r)$ defined in (59) is locally integrable on $[c,\infty[$ for positive $c > 0$, the differential expression τ_ν^ε is regular at $c > 0$. All self-adjoint realizations of τ_ν^ε on $L^2(]c,\infty[,\mathbb{C}^2;dr)$ are restrictions of the maximal operator

$$D(M_{c,\infty}) \;=\; \{\,u \in AC(]c,\infty[,\mathbb{C}^2) \mid \tau_\nu^\varepsilon\,u \in L^2(]c,\infty[,\mathbb{C}^2;dr)\,\}\,,\quad M_{c,\infty}\,u \;=\; \tau_\nu^\varepsilon\,u$$

by means of boundary conditions at $c > 0$. One obtains self-adjoint boundary conditions in terms of vanishing Lagrange brackets, which stem from the Lagrange identity

$$\langle \tau_\nu^\varepsilon\,u(r), v(r)\rangle \;-\; \langle u(r), \tau_\nu^\varepsilon\,v(r)\rangle \;=\; \tfrac{d}{dr}\,[u,v]_r\,, \qquad r \in]0,\infty[$$

for absolutely continuous functions $u, v :]0,\infty[\to \mathbb{C}^2$. The Lagrange identity implies Green's formula

$$\langle M_{c,\infty}\,u, v\rangle_{L^2(]c,\infty[)} - \langle u, M_{c,\infty}\,v\rangle_{L^2(]c,\infty[)} \;=\; \lim_{r\nearrow\infty}\,[u,v]_r - [u,v]_c$$

for all $u, v \in D(M_{c,\infty})$, see Theorem 3.10 in [We87]. The Lagrange bracket for τ_ν^ε is readily calculated as

$$[u,v]_r \;=\; \langle (q - q^*)\,u(r), v(r)\rangle \;=\; i\,\varepsilon\,\overline{u_1(r)}\,v_1(r) - i\,\varepsilon\,\overline{u_2(r)}\,v_2(r)\,.$$

LEMMA 18 (AWAY FROM ZERO) *Let* $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z} + 1/2)$, *and* $c > 0$. *The deficiency indices of the maximal operator* $M_{c,\infty}$ *are both equal one, and all self-adjoint realizations* $A^{\alpha}_{c,\infty}$ *of the differential expression* τ^{ε}_{ν} *in* $L^2(]c,\infty[,\mathbb{C}^2;dr)$ *are given by*

$$D(A^{\alpha}_{c,\infty}) \;=\; \{u \in D(M_{c,\infty}) \mid u_1(c) \;=\; e^{i\alpha} u_2(c)\}, \qquad A^{\alpha}_{c,\infty}\, u \;=\; \tau^{\varepsilon}_{\nu}\, u$$

with $\alpha \in [0, 2\pi[$. *Moreover,* $\sigma(A^{\alpha}_{c,\infty}) = \sigma_{\mathrm{ess}}(A^{\alpha}_{c,\infty}) = \mathbb{R}$ *for all* $\alpha \in [0, 2\pi[$.

PROOF. Recycling some of the arguments already used in the proof of Lemma 15, the deficency indices $\gamma_\pm$ of $M_{c,\infty}$ are easily calculated as

$$\gamma_\pm \;=\; \gamma^\pm_c + \gamma^\pm_\infty - 2 \;=\; 2 + 1 - 2 \;=\; 1\,.$$

Hence, by Theorem 4.9.b in [We87], the domains of the self-adjoint realizations of τ^{ε}_{ν} on $L^2(]c,\infty[,\mathbb{C}^2;dr)$ are characterized by vectors $a = (a_1, a_2) \in \mathbb{C}^2 \setminus \{(0,0)\}$ with

$$[a, a]_c \;=\; i\,\varepsilon\,|a_1|^2 - i\,\varepsilon\,|a_2|^2 \;=\; 0\,,$$

that is with $a_1 = e^{i\alpha} a_2$ for some $\alpha \in [0, 2\pi[$. Thus, the self-adjoint realizations can be parametrized by an angular variable $\alpha \in [0, 2\pi[$ and have as domains

$$\{u \in D(M_{c,\infty}) \mid [a, u]_c \;=\; 0\} \;=\; \{u \in D(M_{c,\infty}) \mid u_1(c) \;=\; e^{i\alpha} u_2(c)\}\,.$$

Employing once more the decay properties of solutions of $(\tau^{\varepsilon}_{\nu} - \lambda)\, u = 0$ with $\lambda \in \mathbb{R}$, which are given by equation (63), we have

$$\gamma_{c,\lambda} + \gamma_{\infty,\lambda} \;=\; 2 + 0 \;<\; 2 + \gamma_\pm \;=\; 2 + 1\,.$$

Hence, the whole real line is essential spectrum for all the operators $A^{\alpha}_{c,\infty}$. □

For the proof of Theorem 9 we will approximate the operators $A^{\alpha}_{c,\infty}$ by a sequence of self-adjoint realizations of τ^{ε}_{ν} on $L^2(]c,R[,\mathbb{C}^2;dr)$ with $R > c$. On bounded intervals $]c,R[$ with $c > 0$ and $R > c$, the differential expression τ^{ε}_{ν} is regular. All self-adjoint realizations of τ^{ε}_{ν} on $L^2(]c,R[,\mathbb{C}^2;dr)$ are restrictions of the maximal operator $M_{c,R}$

$$D(M_{c,R}) \;=\; \{u \in AC(]c,R[,\mathbb{C}^2) \mid \tau^{\varepsilon}_{\nu}\, u \in L^2(]c,R[,\mathbb{C}^2;dr)\}, \quad M_{c,R}\, u \;=\; \tau^{\varepsilon}_{\nu}\, u$$

by means of boundary conditions. However, in the regular case there are plenty of self-adjoint boundary conditions, and we prefer restricting our attention to the separated ones.

LEMMA 19 (SEPARATED BOUNDARY CONDITIONS) *Let* $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z} + 1/2)$, $c > 0$, *and* $c < R < \infty$. *The deficiency indices of the maximal operator* $M_{c,R}$ *are both equal two, and the operators* $A^{\alpha,\beta}_{c,R}$,

$$D(\,A^{\alpha,\beta}_{c,R}\,) \;=\; \{u \in D(M_{c,\infty}) \mid u_1(c) = e^{i\alpha} u_2(c)\,,\, u_1(R) = e^{i\beta} u_2(R)\}, \quad A^{\alpha,\beta}_{c,R}\, u \;=\; \tau^{\varepsilon}_{\nu}\, u$$

with $\alpha, \beta \in [0, 2\pi[$ *are all self-adjoint realizations of* τ^{ε}_{ν} *on* $L^2(]c,R[,\mathbb{C}^2;dr)$ *with separated boundary conditions.*

The operators $A^{\alpha,\beta}_{c,R}$, $\alpha, \beta \in [0, 2\pi[$, *have discrete spectrum with simple eigenvalues* λ_n, $n \in \mathbb{N}$. *Moreover,* $\sum_{\lambda_n \neq 0} \lambda_n^{-2} < \infty$.

PROOF. The deficency indices $\gamma_\pm$ of $M_{c,R}$ are

$$\gamma_\pm \;=\; \gamma_c^\pm + \gamma_R^\pm - 2 \;=\; 2+2-2 \;=\; 2\,.$$

By Theorem 4.10 in [We87], two linearly independent vectors $a, b \in \mathbb{C}^2$ with $[a,a]_c = [b,b]_R = 0$ describe domains of self-adjoint realizations of τ_ν^ε on $L^2(]c,R[,\mathbb{C}^2;dr)$ with separated boundary conditions. The Lagrange bracket condition means

$$a_1 = e^{i\,\alpha}\,a_2\,,\; b_1 = e^{i\,\beta}\,b_2 \quad \text{for some} \quad \alpha, \beta \in [0, 2\pi[\,.$$

Thus, we have two angular variables $\alpha, \beta \in [0, 2\pi[$ and domains

$$\begin{aligned} &\{u \in D(M_{c,R}) \mid [a,u]_c = [b,u]_R = 0\} \\ =\;\; &\{u \in D(M_{c,R}) \mid u_1(c) = e^{i\,\alpha}\,u_2(c)\,,\, u_1(R) = e^{i\,\beta}\,u_2(R)\}\,. \end{aligned}$$

Since p_ν is a smooth function on the interval $]c,R[$, the solutions of $(\tau_\nu^\varepsilon - \lambda)\,u = 0$ for $\lambda \in \mathbb{C}$ lie all in $L^2(]c,R[,\mathbb{C}^2;dr)$. Hence, τ_ν^ε is quasi regular at $c > 0$ and $R > c$. By Theorem 7.11 in [We87], the spectrum of the operators $A_{c,R}^{\alpha,\beta}$ is discrete, and

$$\sum_{\lambda_n \neq 0} \lambda_n^{-2} \;<\; \infty\,.$$

Since every solution of the differential equation $(\tau_\nu^\varepsilon - \lambda)\,u = 0$ is determined by the boundary condition at one of the boundary points up to a constant factor, the eigenvalues are simple. □

Having discussed the boundary conditions, which are relevant for the proof of Theorem 9, we turn to a short recapitulation about spectral representations and spectral matrices.

17.4 SPECTRAL REPRESENTATION

Every self-adjoint operator A in a separable Hilbert space H has an ordered spectral representation. That is, there exists a unitary operator U,

$$U:\; H \to \bigoplus_{j\in I} L^2(\mathbb{R},\mathbb{C};d\sigma_j)\,,$$

such that $U A\, U^*$ is the operator of multiplication by the identity function in the space $\bigoplus_{j\in I} L^2(\mathbb{R},\mathbb{C};d\sigma_j)$. The index set I is countable, and the measures σ_j are finite Borel measures on $\mathbb{R}$ with the property, that the measure σ_{j+1} is absolutely continuous with respect to its predecessor σ_j for all $j \in I$. Given a spectral resolution $E(\cdot)$ of A, the measures σ_j are obtained as

$$\sigma_j(B) \;=\; \|E(B)\,g_j\|_H^2\,, \qquad B \subset \mathbb{R} \quad \text{Borel sets}\,,$$

with suitably chosen $g_j \in H$, see Theorem 8.1 in [We87]. For the self-adjoint realizations A of the ordinary differential expression τ_ν^ε the index set I equals $\{1,2\}$. There is a right-continuous non-decreasing matrix-valued function $\rho_{c,R} : \mathbb{R} \to \mathcal{L}(\mathbb{C}^2)$ uniquely determind by

$\rho_{c,R}(0) = 0$, such that

$$U_{c,R}: \; L^2(]c,R[,\mathbb{C}^2;dr) \to L^2(\mathbb{R},\mathbb{C}^2;d\rho_{c,R}),$$

$$(U_{c,R}\, f)(\lambda) \;=\; \underset{\substack{c'\searrow c\\ R'\nearrow R}}{\mathrm{l.i.m.}} \begin{pmatrix} \int_{c'}^{R'} \langle u_\lambda(r), f(r)\rangle\, dr \\ \int_{c'}^{R'} \langle v_\lambda(r), f(r)\rangle\, dr \end{pmatrix}$$

is a unitary operator with $UA\,U^*$ equal to the multiplication by the identity function in $L^2(\mathbb{R},\mathbb{C}^2;d\rho_{c,R})$. The set $\{u_\lambda, v_\lambda\}$ is a fundamental system of the differential equation $(\tau_\nu^\varepsilon - \lambda)\,u = 0$, and l. i. m. refers to the limit in $L^2(\mathbb{R},\mathbb{C}^2;d\rho_{c,R})$, see Theorem 8.7 in [We87]. Such a unitary operator is also referred to as a spectral representation. Working on intervals $]c,R[$ with $c > 0$ and $c < R \leq \infty$, which are away from the singular point zero, we have spectral matrices $\rho_{c,R}$ of a particularly simple form.

Lemma 20 (Spectral Representation) *Let $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z}+1/2)$, $c > 0$, and choose $R \in]c,\leq\infty[$. Let $A^{\alpha}_{c,\infty}$ and $A^{\alpha,\beta}_{c,R}$ with $\alpha,\beta \in [0,2\pi[$ be the self-adjoint realizations of τ_ν^ε on $L^2(]c,R[,\mathbb{C}^2;dr)$, which have been introduced in Lemma 18 and Lemma 19. Then, all such operators have a spectral matrix $\rho_{c,R}:\mathbb{R}\to\mathbb{C}^{2,2}$ of the form*

$$\rho_{c,R} \;=\; \begin{pmatrix} (\rho_{c,R})_{1,1} & 0 \\ 0 & 0 \end{pmatrix}.$$

There is a Borel measure $\mu_{c,R}$ on $\mathbb{R}$ and a simplified spectral representation

$$U_{c,R}: \; L^2(]c,R[,\mathbb{C}^2;dr) \to L^2(\mathbb{R},\mathbb{C};d\mu_{c,R}), \quad (U_{c,R}\, f)(\lambda) \;=\; \int_c^R \langle u_\lambda(r), f(r)\rangle\, dr,$$

where u_λ is a solution of the differential equation $(\tau_\nu^\varepsilon - \lambda)\,u = 0$ satisfying the boundary condition $u_1(c) = e^{i\,\alpha}\,u_2(c)$. If $R < \infty$, the measure $\mu_{c,R}$ is a pure point measure with

$$\mu_{c,R}(I) \;=\; \sum_{\lambda_n\in I} \|u_{\lambda_n}\|^{-2}_{L^2(]c,R[)}, \qquad I\subset\mathbb{R} \quad \textit{intervals},$$

where $\{\lambda_n \mid n\in\mathbb{N}\} = \sigma(\,A^{\alpha,\beta}_{c,R}\,)$ are the eigenvalues of $A^{\alpha,\beta}_{c,R}$, and u_{λ_n} corresponding eigenfunctions.

Proof. Justifying the claims for the case $R \leq \infty$, we just have to apply Theorem 10.7 in [We87] and its subsequent remarks. There, the asserted form of the spectral representation is proven for self-adjoint realizations with separated boundary conditions for differential expressions τ, which are regular at c, if the solution space of $(\tau-\lambda)\,u = 0$ is two-dimensional, and if $\gamma_c^{\pm} = 2$. For the case $R < \infty$, Lemma 19 yields that the measure $\mu_{c,R}$ must be of the form

$$\mu_{c,R} \;=\; \sum_{n\in\mathbb{N}} \delta_{\lambda_n}\;\mu_n$$

with non-negative weights $\mu_n \geq 0$. Let λ_N be an eigenvalue of $A^{\alpha,\beta}_{c,R}$. Then,

$$(U_{c,R}\,u_{\lambda_N})(\lambda) \;=\; \int_c^R \langle u_\lambda(r), u_{\lambda_N}\rangle\, dr \;=\; \langle u_\lambda, u_{\lambda_N}\rangle_{L^2(dr)}, \qquad \lambda\in\mathbb{R},$$

where u_λ is chosen as an eigenfunction of λ, if $\lambda \in \sigma(A^{\alpha,\beta}_{c,R})$. Since $U_{c,R}$ is unitary, and since eigenfunctions for different eigenvalues are orthogonal, we have

$$\|u_{\lambda_N}\|^2_{L^2(dr)} = \|U_{c,R}\, u_{\lambda_N}\|^2_{L^2(d\mu_{c,R})} = \sum_{n\in\mathbb{N}} |\langle u_{\lambda_n}, u_{\lambda_N}\rangle_{L^2(dr)}|^2\, \mu_n = \|u_{\lambda_N}\|^4_{L^2(dr)}\, \mu_N\,,$$

and therefore $\mu_N = \|u_{\lambda_N}\|^{-2}_{L^2(dr)}$. □

Varying the boundary conditions at $c > 0$, when working on intervals $]c,\infty[$, gives a spectral averaging result analogous to the ones for Schrödinger, Sturm-Liouville, or Dirac differential expressions, see [Ko] and [We96].

Proposition 9 (Spectral Averaging) *Let $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z}+1/2)$, and $c > 0$. Let $A^\alpha_{c,\infty}$ with $\alpha \in [0,2\pi[$ be the self-adjoint realizations of τ^ε_ν in $L^2(]c,\infty[,\mathbb{C}^2;dr)$ and $\mu^\alpha_{c,\infty}$ the associated spectral measures introduced in Lemma 20. Then, the averaged measure*

$$\int_0^{2\pi} \mu^\alpha_{c,\infty}\, d\alpha$$

is absolutely continuous with respect to Lebesgue measure on $\mathbb{R}$.

After computation of a Weyl-Titchmarsh m-coefficient for τ^ε_ν, the proof uses arguments analogous to the ones of Theorem 2 in [We96], which shows a spectral averaging result for Jacobi matrices.

Proof. Let $\{u_1, u_2\}$ be a fundamental system of $(\tau^\varepsilon - z)\, u = 0$ with $z \in \mathbb{C}$. Then, all solutions of the inhomogeneous problem $(\tau^\varepsilon_\nu - z)\, u = f$ with $f \in L^1_{loc}(]c,\infty[,\mathbb{C}^2;dr)$ have the form

$$\begin{aligned} u(r) &= a_1\, u_1(r) + a_2\, u_2(r) + u_1(r) \int_d^r W(u_1,u_2,y)^{-1} W([f],u_2,y)\, dy \\ &+ u_2(r) \int_d^r W(u_1,u_2,y)^{-1} W(u_1,[f],y)\, dy \end{aligned}$$

with $d \in]c,\infty[$, see Theorem 5.2 in [We87]. Though τ^ε_ν is not real, an elementary computation yields that the Wronskian $W(u_1,u_2,y) = \det(u_1(y),u_2(y)) = W(u_1,u_2)$ is constant. The modified Wronskians are

$$W([f],u_2,y) := \det((q-q^*)^{-1} f(y), u_2(y)) = \tfrac{i}{\varepsilon}\,(f_1(y)\, u_{2,2}(y) + f_2(y)\, u_{2,1}(y))$$

and

$$W(u_1,[f],y) := \det(u_1(y), (q-q^*)^{-1} f(y)) = -\tfrac{i}{\varepsilon}\,(u_{1,1}(y) f_2(y) + u_{1,2}(y)\, f_1(y))\,.$$

Hence,

$$\begin{aligned} u(r) &= a_1\, u_1(r) + a_2\, u_2(r) + \tfrac{i}{\varepsilon}\, W(u_1,u_2)^{-1} \Bigg(u_1(r) \int_d^r \langle\, \overline{(u_{2,2}(y), u_{2,1}(y))^t}, f(y)\,\rangle\, dy \\ &- u_2(r) \int_d^r \langle\, \overline{(u_{1,2}(y), u_{1,1}(y))^t}, f(y)\,\rangle\, dy \Bigg)\,. \end{aligned}$$

We choose two solutions $u^\alpha(z;\cdot)$ and $v^\alpha(z;\cdot)$ of $(\tau_V^\varepsilon - z)\,u = 0$ with boundary values at $c > 0$

$$u^\alpha(z;c) \;=\; (e^{i\,\alpha},1)^t\,, \qquad v^\alpha(z;c) \;=\; (i/\varepsilon,0)^t\,,$$

such that

$$-\tfrac{i}{\varepsilon}\,W(u^\alpha(z;\cdot),v^\alpha(z;\cdot))^{-1} \;=\; 1\,.$$

Since the deficiency indices $\gamma_\pm$ of $A^\alpha_{c,\infty}$ equal one, there exists for every $z \in \mathbb{C}\setminus\mathbb{R}$ a unique coefficient $m^\alpha(z) \in \mathbb{C}$, the Weyl-Titchmarsh m-coefficient, with

$$m^\alpha(z)\,u^\alpha(z;\cdot) + v^\alpha(z;\cdot) \;=:\; w_\infty(z;\cdot) \in L^2(]c,\infty[,\mathbb{C}^2;dr)\,.$$

Setting $w_c(z;\cdot) := u^\alpha(z;\cdot)$, we have $-\frac{i}{\varepsilon}\,W(w_c(z;\cdot),w_\infty(z;\cdot))^{-1} \;=\; 1$, and Theorem 7.3 in [We87] yields the resolvent as

$$\begin{aligned}(A^\alpha_{c,\infty} - z)^{-1}f(r) \;&=\; w_c(z;r)\int_r^\infty \langle\, \overline{(w_{\infty,2}(z;y),w_{\infty,1}(z;y))^t}, f(y)\,\rangle\,dy \\ &+\; w_\infty(z;r)\int_c^r \langle\, \overline{(w_{c,2}(z;y),w_{c,1}(z;y))^t}, f(y)\,\rangle\,dy\end{aligned}$$

for $f \in L^2(]c,\infty[,\mathbb{C}^2;dr)$. Since $\overline{(u_2^\alpha(z;\cdot),u_1^\alpha(z;\cdot))^t}$ and $\overline{(v_2^\alpha(z;\cdot),v_1^\alpha(z;\cdot))^t}$ are solutions of $(\tau_V^\varepsilon - \overline{z})\,u = 0$, both of them must be linear combinations of $u^\alpha(\overline{z};\cdot)$ and $v^\alpha(\overline{z};\cdot)$. Inserting the boundary values at $c > 0$, we obtain

$$\overline{(u_2^\alpha(z;\cdot),u_1^\alpha(z;\cdot))^t} \;=\; e^{-i\,\alpha}\,u^\alpha(\overline{z};\cdot)\,, \qquad \overline{(v_2^\alpha(z;\cdot),v_1^\alpha(z;\cdot))^t} \;=\; -\tfrac{i}{\varepsilon}\,u^\alpha(\overline{z};\cdot) + e^{i\,\alpha}\,v^\alpha(\overline{z};\cdot)$$

and for the resolvent

$$\begin{aligned}(A^\alpha_{c,\infty} - z)^{-1}f(r) \;&=\; u^\alpha(z;r)\int_r^\infty \langle\, (\,\overline{m^\alpha(z)}\,e^{-i\,\alpha} - \tfrac{i}{\varepsilon}\,)\,u^\alpha(\overline{z};y) + e^{i\,\alpha}\,v^\alpha(\overline{z};y), f(y)\,\rangle\,dy \\ &+\; (m^\alpha(z)\,u^\alpha(z;r) + v^\alpha(z;\cdot))\int_c^r \langle\, e^{-i\,\alpha}\,u^\alpha(\overline{z};y), f(y)\,\rangle\,dy\,.\end{aligned}$$

With the notation of Chapter 9 in [We87] this means

$$m_{11}^+(z) \;=\; m^\alpha(z)\,e^{i\,\alpha}\,, \quad m_{12}^+(z) \;=\; 0\,, \quad m_{21}^+(z) \;=\; e^{i\,\alpha}\,, \quad m_{22}^+(z) \;=\; 0\,,$$

and

$$m_{11}^-(z) \;=\; m^\alpha(z)\,e^{i\,\alpha} + \tfrac{i}{\varepsilon}\,, \quad m_{12}^-(z) \;=\; e^{-i\,\alpha}\,, \quad m_{21}^-(z) \;=\; 0\,, \quad m_{22}^-(z) \;=\; 0\,.$$

We obtain by the Weyl-Titchmarsh-Kodaira formula, Corollary 9.5 in [We87], a spectral matrix of the form given in Lemma 20 with upper left component

$$(\rho^\alpha_{c,\infty})_{1,1}\,(\lambda) \;=\; (2\pi i)^{-1}\,e^{i\,\alpha}\,\lim_{\delta'\searrow 0}\,\lim_{\delta\searrow 0}\int_{\delta'}^{\lambda+\delta'} (m^\alpha(t+i\,\delta) - m^\alpha(t-i\,\delta))\,dt$$

for $\lambda \in \mathbb{R}$. Since $\sigma_p(A^\alpha_{c,\infty}) = \emptyset$, the spectral measure $\mu^\alpha_{c,\infty}$ is

$$\mu^\alpha_{c,\infty}(I) \;=\; (2\pi i)^{-1}\,e^{i\,\alpha}\,\lim_{\delta\searrow 0}\int_I (m^\alpha(t+i\,\delta) - m^\alpha(t-i\,\delta))\,dt$$

for intervals $I \subset \mathbb{R}$. By Lemma 9.1 of [We87], we have $m^+_{11}(\bar z) = \overline{m^-_{11}(z)}$ for all $z \in \mathbb{C} \setminus \mathbb{R}$, and hence

$$\mu^\alpha_{c,\infty}(I) \;=\; \pi^{-1} \lim_{\delta \searrow 0} \int_I \big(\mathrm{Im}(m^\alpha(t + i\,\delta)\, e^{i\,\alpha}) + (2\varepsilon)^{-1}\big)\, dt\,.$$

Since $(\tau^\varepsilon_\nu - z)\, w_\infty(z;\cdot) = 0$ for $z \in \mathbb{C} \setminus \mathbb{R}$, Green's formula implies

$$\begin{aligned}
&2\,i\,\mathrm{Im}(z) \int_c^\infty |w_\infty(z;r)|^2\, dr \\
&= \; -\int_c^\infty (\, \langle \tau^\varepsilon_\nu\, w_\infty(z;r), w_\infty(z;r)\rangle - \langle w_\infty(z;r), \tau^\varepsilon_\nu\, w_\infty(z;r)\rangle\,)\, dr \\
&= \; [w_\infty(z,\cdot), w_\infty(z,\cdot)]_c \;=\; 2\,i\,\mathrm{Im}(m^\alpha(z)\, e^{i\,\alpha}) + \tfrac{i}{\varepsilon}
\end{aligned}$$

and

$$\mathrm{Im}(m^\alpha(t + i\,\delta)\, e^{i\,\alpha}) + (2\varepsilon)^{-1} \;>\; 0 \qquad \text{for all} \qquad t \in \mathbb{R}\,.$$

Since $\gamma_\pm = 1$, we have for every $z \in \mathbb{C} \setminus \mathbb{R}$ a constant $c^\alpha(z) \in \mathbb{C}$ with

$$c^\alpha(z)\,(\, m^0(z)\, u^0(z,\cdot) + v^0(z,\cdot)\,) \;=\; m^\alpha(z)\, u^\alpha(z,\cdot) + v^\alpha(z,\cdot)\,.$$

Evaluating the previous equation at the boundary point $c > 0$, we obtain

$$c^\alpha(z)\, m^0(z) \;=\; m^\alpha(z)\,.$$

If $m^0(z) \;=\; 0$, then $m^\alpha(z) \;=\; 0$ for all $\alpha \in [0, 2\pi[$, and $\int_0^{2\pi} m^\alpha(z)\, d\alpha = 0$. Otherwise,

$$c^\alpha(z) \;=\; m^\alpha(z)\, m^0(z)^{-1}$$

and

$$m^\alpha(z)(\,1 - e^{i\,\alpha} + \tfrac{i}{\varepsilon}\, m^0(z)^{-1}\,) \;=\; \tfrac{i}{\varepsilon}\,.$$

Hence,

$$[0, 2\pi] \;\to\; \mathbb{C}\,, \quad \alpha \;\mapsto\; m^\alpha(z)\, e^{i\,\alpha} \;=\; \varepsilon^{-1}\; i\, e^{i\,\alpha}\, \big(1 - e^{i\,\alpha} + \tfrac{i}{\varepsilon}\, m^0(z)^{-1}\big)^{-1}$$

is a smooth function with

$$\begin{aligned}
\int_0^{2\pi} m^\alpha(z)\, e^{i\,\alpha}\, d\alpha \;&=\; \varepsilon^{-1} \int_0^{2\pi} i\, e^{i\,\alpha}\, \big(1 - e^{i\,\alpha} + \tfrac{i}{\varepsilon}\, m^0(z)^{-1}\big)^{-1}\, d\alpha \\
&=\; -\varepsilon^{-1}\, \ln\big(1 - e^{i\,\alpha} + \tfrac{i}{\varepsilon}\, m^0(z)^{-1}\big)\Big|_{\alpha=0}^{2\pi} \;=\; 0\,.
\end{aligned}$$

By Fatou's Lemma and Fubini's Theorem, we obtain for every bounded interval $I \subset \mathbb{R}$

$$\begin{aligned}
\int_0^{2\pi} \mu^\alpha_{c,\infty}(I)\, d\alpha \;&=\; \pi^{-1} \int_0^{2\pi} \lim_{\delta \searrow 0} \int_I \big(\mathrm{Im}(m^\alpha(t + i\,\delta)\, e^{i\,\alpha}) + (2\varepsilon)^{-1}\big)\; dt\, d\alpha \\
&\leq\; \pi^{-1} \liminf_{\delta \searrow 0} \int_0^{2\pi} \int_I \big(\mathrm{Im}(m^\alpha(t + i\,\delta)\, e^{i\,\alpha}) + (2\varepsilon)^{-1}\big)\; dt\, d\alpha \\
&=\; \pi^{-1} \liminf_{\delta \searrow 0} \int_I \int_0^{2\pi} \big(\mathrm{Im}(m^\alpha(t + i\,\delta)\, e^{i\,\alpha}) + (2\varepsilon)^{-1}\big)\; d\alpha\, dt \;=\; \varepsilon^{-1}\, |I|\,.
\end{aligned}$$

□

Having the necessary information about self-adjoint boundary conditions and spectral representations at hand, we now turn to the proof of the absolutely continuous spectrum.

17.5 Proof of Absolutely Continuous Spectrum

We prove Theorem 9, that is $\sigma(M^\varepsilon_\nu) = \sigma_{ac}(M^\varepsilon_\nu) = \mathbb{R}$ for all $\varepsilon > 0$ and all $\nu \in \varepsilon(\mathbb{Z} + 1/2)$.

Proof. We proceed in four steps. First, one approximates by auxiliary problems defined on intervals $]c, \infty[$ and $]c, R[$. Second, one bounds the variation of the corresponding spectral matrices by means of the uniform non-subordinacy condition. Third, one bounds these variations by means of the spectral measure associated with the problem on some interval $]c_0, \infty[$. Fourth, one uses the spectral averaging result to conclude the proof.

First step. We approximate M^ε_ν by the sequence $(A^0_{c,\infty})_{c>0}$ in the sense of generalized strong convergence. That is, if we denote by $P_{c,\infty} : L^2(]0, \infty[, \mathbb{C}^2; dr) \to L^2(]c, \infty[, \mathbb{C}^2; dr)$ the orthogonal projections in $L^2(]0, \infty[, \mathbb{C}^2; dr)$ onto $L^2(]c, \infty[, \mathbb{C}^2; dr)$, then we have

$$(A^0_{c,\infty} - z)^{-1} P_{c,\infty} \;\to\; (M^\varepsilon_\nu - z)^{-1} \quad \text{strongly as} \quad c \searrow 0 \quad \text{for all} \quad z \in \mathbb{C} \setminus \mathbb{R} .$$

The convergence proof is literally the same as the one for Sturm-Liouville expressions and Dirac systems given in Theorem 6 of [StWe]. Analogously for every $c > 0$, we approximate $A^0_{c,\infty}$ by the sequence $(A^{0,0}_{c,R})_{R>c}$ as $R \nearrow \infty$. Since $\sigma_p(M^\varepsilon_\nu) = \sigma_p(A^0_{c,\infty}) = \emptyset$, the generalized strong convergence implies strong convergence of the spectral resolutions $E(\cdot)(\lambda)$, that is

$$E(A^0_{c,\infty})(\lambda) P_{c,\infty} \;\to\; E(M^\varepsilon_\nu)(\lambda) \quad \text{strongly as} \quad c \searrow 0 \quad \text{for all} \quad \lambda \in \mathbb{R} ,$$

and for all $c > 0$

$$E(A^0_{c,R})(\lambda) P_{c,R} \;\to\; E(A^{0,0}_{c,\infty})(\lambda) P_{c,\infty} \quad \text{strongly as} \quad R \nearrow \infty \quad \text{for all} \quad \lambda \in \mathbb{R} .$$

Let $c_0 > 0$, and let $\{u_\lambda, v_\lambda\}$ be a fundamental system of $(\tau^\varepsilon_\nu - \lambda)\, u = 0$ for all $\lambda \in \mathbb{R}$ with

$$u_\lambda(c_0) \;=\; (1, 0)^t , \qquad v_\lambda(c_0) \;=\; (0, 1)^t .$$

Then, the convergence of the spectral resolutions translates into convergence of the spectral matrices associated with $\{u_\lambda, v_\lambda\}$. That is,

$$\lim_{c \searrow 0} \left(\rho_{c,\infty}(\lambda) - \rho_{c,\infty}(\lambda')\right) \;=\; \rho(\lambda) - \rho(\lambda') ,$$

and

$$\lim_{R \nearrow \infty} \left(\rho_{c,R}(\lambda) - \rho_{c,R}(\lambda')\right) \;=\; \rho_{c,\infty}(\lambda) - \rho_{c,\infty}(\lambda') \tag{65}$$

for all $\lambda, \lambda' \in \mathbb{R}$, see Theorem 14.13 in [We02].

Second Step. Since the spectrum $\sigma(\, A^{0,0}_{c,R}\,) \;=\; \{\lambda_n \mid n \in \mathbb{N}\}$ of $A^{0,0}_{c,R}$ is point spectrum only, the mapping $\lambda \mapsto \rho_{c,R}(\lambda)$ is a jump function, which is constant on the intervals without eigenvalues. Let λ be an eigenvalue, ϕ_λ the eigenfunction with $|\phi_\lambda(c_0)| = 1$, and $\Delta_{c,R}(\lambda) = \rho_{c,R}(\lambda) - \rho_{c,R}(\lambda - 0)$ the corresponding jump. Then, we have for all $f, g \in L^2(]c, R[, \mathbb{C}^2; dr)$

$$\begin{aligned} \langle (U_{c,R}\, f)(\lambda), \Delta_{c,R}(\lambda)(U_{c,R}\, g)(\lambda) \rangle \;&=\; \langle\, f, E(A^{0,0}_{c,R})(\{\lambda\}) g\, \rangle_{L^2(]c,R[)} \\ &=\; \|\phi_\lambda\|^{-2}_{L^2(]c,R[)} \, \langle f, \phi_\lambda \rangle_{L^2(]c,R[)} \, \langle \phi_\lambda, g \rangle_{L^2(]c,R[)} \; . \end{aligned}$$

By construction of the unitary operator $U_{c,R}$, we obtain for the elements of the jump matrix $\Delta_{c,R}(\lambda)$

$$(\Delta_{c,R})_{k,l}(\lambda) \;=\; \|\varphi_\lambda\|^{-2}_{L^2(]c,R[)}\, \varphi_{\lambda,k}(c_0)\,\overline{\varphi_{\lambda,l}(c_0)}\,, \qquad k,l\in\{1,2\}\,.$$

Let $I\subset\mathbb{R}$ be a compact interval, θ and $k(\cdot)$ the constants of the uniform non-subordinacy condition provided by Lemma 17. We get for the variation of the matrix components of $\lambda\mapsto\rho_{c,R}(\lambda)$ on I

$$\operatorname*{var}_{I}\,(\rho_{c,R})_{k,l} \;\le\; \sum_{\lambda_n\in I}\|\Delta_{c,R}(\lambda_n)\| \;\le\; \sum_{\lambda_n\in I}\|\varphi_{\lambda_n}\|^{-2}_{L^2(]c,R[)} \;\le\; \sharp(\sigma(\,A^{0,0}_{c,R})\cap I)\,(\theta\,k(R))^{-1}$$

with $k,l\in\{1,2\}$. There is a constant $C_c\in\mathbb{Z}$ just depending on $c>0$ such that

$$\sharp(\sigma(\,A^{0,0}_{c,R})\cap I) \;=\; \sharp(\sigma(\,A^{0,0}_{c_0,R})\cap I)+C_c\,.$$

Since $k(R)\to\infty$ as $R\nearrow\infty$, we have by the limit established in equation (65) that

$$\operatorname*{var}_{I}\,(\rho_{c,\infty})_{k,l} \;\le\; \limsup_{R\nearrow\infty}\,\operatorname*{var}_{I}\,(\rho_{c,R})_{k,l} \;\le\; \limsup_{R\nearrow\infty}\,\sharp(\sigma(\,A^{0,0}_{c_0,R})\cap I)\,(\theta\,k(R))^{-1}\,.$$

Third Step. From the limit in equation (65) we deduce for the spectral measures, which have been introduced in Lemma 20, that

$$\lim_{R\nearrow\infty}\,\mu_{c_0,R}(I) \;=\; \mu_{c_0,\infty}(I) \tag{66}$$

for all bounded intervals $I\subset\mathbb{R}$. Let $\{\sigma_n\mid n\in\mathbb{N}\}=\sigma(A^{0,0}_{c_0,R})$, and denote by u_{σ_n} an eigenfunction of σ_n. For compact intervals $I\subset\mathbb{R}$ and $R>c_0$ we have by the non-subordinacy bounds of Lemma 17

$$\mu_{c_0,R}(I) \;=\; \sum_{\sigma_n\in I}\|u_{\sigma_n}\|^{-2}_{L^2(]c_0,R[)} \;\ge\; \sharp(\sigma(\,A^{0,0}_{c_0,R})\cap I)\,k(R)^{-1}\,,$$

and therefore

$$\mu_{c_0,\infty}(I) \;\ge\; \limsup_{R\nearrow\infty}\sharp(\sigma(\,A^{0,0}_{c_0,R})\cap I)\,k(R)^{-1}\,.$$

Hence,

$$\operatorname*{var}_{I}\,(\rho_{c,\infty})_{k,l} \;\le\; \theta^{-1}\mu_{c_0,\infty}(I)\,.$$

Fourth Step. We consider the self-adjoint realizations $A^{\alpha}_{c,\infty}$ of τ^{ε}_{V} on $L^2(]c,\infty[,\mathbb{C}^2;dr)$ with $c>0$. We denote the associated spectral measures by $\mu^{\alpha}_{c,\infty}$ with $\alpha\in[0,2\pi[$. With this notation, the measure $\mu_{c_0,\infty}$ used in the previous step is identical $\mu^{0}_{c_0,\infty}$. From the representation of resolvents used in the proof of Lemma 9, we deduce continuity of the mapping $\alpha\mapsto(A^{\alpha,0}_{c,R}-z)^{-1}$ for $z\in\mathbb{C}\setminus\mathbb{R}$. Hence, for all intervals $I\subset\mathbb{R}$ there exists a constant $C_{c,R}(I)\ge 0$ such that

$$|\,\sharp(\sigma(\,A^{\alpha,0}_{c,R})\cap I)-C_{c,R}(I)\,|\le\;1 \qquad \text{for all}\quad \alpha\in[0,2\pi[\,.$$

Again by the non-subordinacy bounds of Lemma 17, we have for compact intervals $I\subset\mathbb{R}$

$$(C_{c,R}(I)-1)\,k(R)^{-1} \;\le\; \mu^{\alpha}_{c,R}(I) \;\le\; (C_{c,R}(I)+1)\,(\theta k(R))^{-1}$$

for all $\alpha \in [0, 2\pi[$. By convergence of the spectral measures, see the limit in equation (66), these inequalities imply

$$\limsup_{R\nearrow\infty} C_{c,R}(I)\, k(R)^{-1} \;\le\; \mu^{\alpha}_{c,\infty}(I) \;\le\; \limsup_{R\nearrow} C_{c,R}(I)\, (\theta k(R))^{-1}$$

for all $\alpha \in [0, 2\pi[$, and therefore

$$\theta\, \mu^{\beta}_{c,\infty}(I) \;\le\; \mu^{\alpha}_{c,\infty}(I) \;\le\; \theta^{-1}\, \mu^{\beta}_{c,\infty}(I)$$

for all $\alpha, \beta \in [0, 2\pi[$. From this we deduce, the equivalence of the measures $\mu^{\alpha}_{c,\infty}$ for $\alpha \in [0, 2\pi[$ on compact intervals. By Proposition 9, the averaged measure

$$\int_0^{2\pi} \mu^{\alpha}_{c,\infty}\, d\alpha$$

is absolutely continuous with respect to Lebesgue measure on $\mathbb{R}$. Hence, the measure $\mu^{0}_{c_0,\infty}$ is absolutely continuous with respect to Lebesgue measure on $\mathbb{R}$. Hence,

$$\operatorname*{var}_{I}(\rho)_{k,l} \;\le\; \limsup_{c\searrow 0} \operatorname*{var}_{I}(\rho_{c,\infty})_{k,l} \;\le\; \theta^{-1}\mu_{c_0,\infty}(I)$$

for compact intervals $I \subset \mathbb{R}$. Therefore, the restriction of the measure ρ to compact intervals $I \subset \mathbb{R}$ is absolutely continuos with respect to Lebesgue measure, which implies absolute continuity of the measure ρ itself, concluding the proof. □

17.6 Immediate Implications

We note, that the fourth step of the proof has shown absolutely continuous spectrum also for the self-adjoint realizations of τ^{ε}_{ν} on $L^2(]c, \infty[, \mathbb{C}^2; dr)$ with $c > 0$.

Corollary 4 *Let $\varepsilon > 0$, $\nu \in \varepsilon(\mathbb{Z}+1/2)$, and $c > 0$. The self-adjoint realizations $A^{\alpha}_{c,\infty}$ of the differential expression τ^{ε}_{ν} in $L^2(]c, \infty[, \mathbb{C}^2; dr)$ have the whole real line as absolutely continuous spectrum, that is*

$$\sigma(A^{\alpha}_{c,\infty}) \;=\; \sigma_{ac}(A^{\alpha}_{c,\infty}) \;=\; \mathbb{R}$$

for all $\alpha \in [0, 2\pi[$.

In Section 15, we have shown that the linear conical crossing Hamiltonian $\overline{H^{\varepsilon}}$ is unitarily equivalent to the orthogonal sum of ordinary differential operators M^{ε}_{ν}, $\nu \in \varepsilon(\mathbb{Z}+1/2)$. By Lemma 7 in the Appendix of [Sch], we have

$$\sigma_{ac}\big(\overline{H^{\varepsilon}}\big) \;=\; \overline{\bigcup_{\nu\in\varepsilon(\mathbb{Z}+1/2)} \sigma_{ac}\big(M^{\varepsilon}_{\nu}\big)}\,.$$

Thus, we have finally proven absolutely continuous spectrum also for the partial differential operator H^{ε}.

Theorem 10 *For all $\varepsilon > 0$, we have $\sigma\big(\overline{H^{\varepsilon}}\big) = \sigma_{ac}\big(\overline{H^{\varepsilon}}\big) = \mathbb{R}$.*

Part E

Appendix

18 Operator Splitting

We denote by A the semi-classical Laplacian $-\frac{\varepsilon^2}{2}\Delta$ acting on $D(A) = H^2(\mathbb{R}^2, \mathbb{C}^2)$ and by B multiplication with the linear potential

$$B: \psi \mapsto V(q)\psi = \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix} \psi$$

acting on $D(B) = \{\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2) \mid |q|\,\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)\}$. Since $V(q)$ is a real symmetric matrix, the domain $D((H^\varepsilon)^*)$ of the adjoint of the model Hamiltonian $H^\varepsilon = -\frac{\varepsilon^2}{2}\Delta + V(q)$ contains the set $D(A) \cap D(B)$. Therefore, H^ε is also essentially self-adjoint on $D(A) \cap D(B)$, and the Trotter product formula, for example Theorem VIII.31 in [ReSi1], gives

$$\exp\big(-\tfrac{it}{\varepsilon}\big(-\tfrac{\varepsilon^2}{2}\Delta + V(q)\big)\big) = s - \lim_{M\to\infty} \big(\exp(-\tfrac{it}{\varepsilon M}\,A)\exp(-\tfrac{it}{\varepsilon M}\,B)\big)^M$$

uniformly on bounded time intervals $J \subset \mathbb{R}$. That is, if we set $\Delta_t = \frac{t}{M}$ and

$$T^\varepsilon_{\Delta_t} := \exp(-\tfrac{i}{\varepsilon}\,\Delta_t\,A)\exp(-\tfrac{i}{\varepsilon}\,\Delta_t\,B)\,,$$

then $\big((T^\varepsilon_{\Delta_t})^M\,\psi^\varepsilon_0\big)_{M\in\mathbb{N}}$ converges to the solution $\psi^\varepsilon(t)$ of the Schrödinger system (1) in $C(J, L^2(\mathbb{R}^2, \mathbb{C}^2))$ as the number of timesteps $M \to \infty$ tends to infinity. To obtain a convergence rate, however, we can no more allow for general initial data $\psi^\varepsilon_0 \in L^2(\mathbb{R}^2, \mathbb{C}^2)$, but have to assume additional regularity and decay properties of the initial data. The literature on product formulae does not cover the case of semi-classically scaled operators and hence does not discuss the dependence of the convergence rate on the semi-classical parameter ε. However, using an operator splitting as reference solver for the surface hopping algorithm, whose validity has only been proven in the limit $\varepsilon \to 0$, the explicit ε-dependance of the splitting's convergence rate is important. Moreover, dealing with a potential, which has an

unbounded negative eigenvalue,

the available results on unbounded operator splitting do not apply either. The analysis of T. Jahnke and C. Lubich in [JaLu00], for example, requires a bound of the form $\|Vf\| \le \text{const.}\|(-\Delta)^{\frac{1}{2}}f\|$, which is not satisfied by our linear potential V, while the results of T. Ichinose et al. [ITTZ], for example, only apply to non-negative operators. Thus, in the following we provide proofs of the convergence rate of Trotter and Strang splitting schemes applied to the semi-classical Schrödinger equation (1). Following the standard approach, these proofs morally treat the potential V as a perturbation of the semi-classical Laplacian $-\frac{\varepsilon^2}{2}\Delta$ and reformulate the problem as an integral equation. Bounding the integrand employs Taylor expansions and commutator bounds. Since bounding of commutators is repeatedly required in the subsequent proofs, we formally recall the standard argument to obtain such bounds.

Let S and T be self-adjoint operators, $U^\varepsilon_T(t)$ a shorthand for the semi-classically scaled one-parameter group $\exp(-\frac{i}{\varepsilon}\,t\,T)$. Formally, without any considerations of domain issues, we have

$$[S, U^\varepsilon_T(t)] = U^\varepsilon_T(t)\int_0^t \tfrac{d}{d\tau}\,(U^\varepsilon_T(-\tau)\,S\,U^\varepsilon_T(\tau))\,d\tau = \tfrac{i}{\varepsilon}\,U^\varepsilon_T(t)\int_0^t U^\varepsilon_T(-\tau)\,[T,S]\,U^\varepsilon_T(\tau)\,d\tau\,,$$

and therefore the bound

$$\|[S, U^\varepsilon_T(t)]\psi\| \;\le\; \tfrac{|t|}{\varepsilon} \sup_{\tau\in[0,t]} \|[S,T]\, U^\varepsilon_T(\tau)\psi\| \,.$$

A less formal observation, also used in the following, is concerned with invariance under time evolution. The unitary evolution associated with a self-adjoint operator leaves the operator's domain invariant, see Lemma VIII.1.7 in [DuSc]. This invariance property also holds for the domains of arbitrary powers of the operator.

LEMMA 21 *Let* S *be a self-adjoint operator with domain* $D(S)$ *and associated strongly continuous one-parameter group* $U(t)$. *Then,* $U(t) : D(S^n) \to D(S^n)$ *for all* $t \in \mathbb{R}$ *and* $n \ge 1$, *where* $S^n = S \circ S^{n-1}$ *and* $D(S^n) = \{\psi \in D(S^{n-1}) \mid S^{n-1}\psi \in D(S)\}$.

PROOF. We only prove the case $n = 2$, since the assertion for higher powers follows then by induction. Let $\psi \in D(S^2)$, that is $\psi, S\psi \in D(S)$. By Lemma VIII.1.7 in [DuSc] we have $U(t)\psi \in D(S)$. Thus, it remains to show $S\,U(t)\psi \in D(S)$, which is equivalent to $s \mapsto U(s)\,S\,U(t)\psi$ being differentiable at $s = 0$. Since S commutes with $U(\cdot)$, $\lim_{s\to 0} \frac{1}{s}\,(U(s)\,S\,U(t)\psi - S\,U(t)\psi)$ exists, and we are done. □

18.1 Trotter Splitting

The following proposition provides the expected convergence rate for the Trotter splitting operator $T^\varepsilon_{\Delta_t}$, which is quadratic in the ratio of timestep Δ_t and semi-classical parameter ε.

PROPOSITION 10 (TROTTER SPLITTING) *For all parameters* $\varepsilon > 0$ *and for all wave functions* $\psi \in \mathcal{H}^4_2 := \{\psi \in H^4(\mathbb{R}^2,\mathbb{C}^2) \mid |q|^2\,\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)\}$ *there exists a positive constant* $C^\varepsilon_\psi > 0$, *such that for all time steps* $\Delta_t \in \mathbb{R}$

$$\left\| \exp(-\tfrac{i}{\varepsilon}\,\Delta_t\,(-\tfrac{\varepsilon^2}{2}\Delta + V))\psi - T^\varepsilon_{\Delta_t}\psi \right\|_{L^2(\mathbb{R}^2)} \;\le\; C^\varepsilon_\psi\,\Delta_t^2 \,.$$

For $\psi \in \mathcal{H}^6_3 := \{\psi \in H^6(\mathbb{R}^2,\mathbb{C}^2) \mid |q|^3\,\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)\}$ *we have*

$$C^\varepsilon_\psi \;=\; \text{const.}\;\varepsilon^{-2} \sum_{k+l=0}^{2} \|A^k\,B^l\,\psi\|_{L^2(\mathbb{R}^2)} \,.$$

PROOF. In the following, we denote

$$(A+B)\psi \;=\; H^\varepsilon\psi\,, \qquad D(A+B) = D\left(\overline{H^\varepsilon}\right) \,.$$

Moreover, for notational simplicity we also use the symbol $\le_c$ to indicate that the right handside of an inequality has to be read modulo a multiplicative constant, which does neither depend on the semi-classical parameter ε nor on the wave function ψ.

First Step. We have $\mathcal{H}^4_2 \subset D((A+B)^2) =: D_2$. We define $V^\varepsilon(\tau) \;=\; U^\varepsilon_B(\Delta_t - \tau)\,U^\varepsilon_{A+B}(\tau)$. By Lemma 21, $U^\varepsilon_{A+B}(\tau)$ leaves D_2 invariant, and thus $\tau \mapsto V^\varepsilon(\tau)\psi$ is differentiable with respect to τ for $\psi \in \mathcal{H}^4_2$. We have

$$\tfrac{d}{d\tau}\,V^\varepsilon(\tau) \;=\; -\tfrac{i}{\varepsilon}\,U^\varepsilon_B(\Delta_t - \tau)\;A\;U^\varepsilon_{A+B}(\tau) \quad \text{on} \quad D_2 \,.$$

Integrating from 0 to Δ_t, we get

$$U^\varepsilon_{A+B}(\Delta_t) \;=\; U^\varepsilon_B(\Delta_t) - \tfrac{i}{\varepsilon}\int_0^{\Delta_t} U^\varepsilon_B(\Delta_t-\tau)\, A\, U^\varepsilon_{A+B}(\tau)\, d\tau\,.$$

On the other hand, we have on $D(A)$

$$U^\varepsilon_A(\Delta_t) \;=\; \mathrm{Id} - \tfrac{i}{\varepsilon}\int_0^{\Delta_t} A\, U^\varepsilon_A(\tau)\, d\tau\,.$$

Since B is multiplication by a linear matrix, $U^\varepsilon_B(\Delta_t)$ means multiplication by a bounded, smooth function with bounded derivatives. Thus, $U^\varepsilon_B(\Delta_t)$ leaves $D(A)$ invariant, and we obtain

$$T^\varepsilon_{\Delta_t} \;=\; U^\varepsilon_B(\Delta_t) - \tfrac{i}{\varepsilon}\int_0^{\Delta_t} A\, U^\varepsilon_A(\tau)\, U^\varepsilon_B(\Delta_t)\, d\tau\,.$$

This gives on $\mathcal{H}^4_2$

$$U^\varepsilon_{A+B}(\Delta_t) - T^\varepsilon_{\Delta_t} \;=\; \tfrac{i}{\varepsilon}\int_0^{\Delta_t} R^\varepsilon(\Delta_t,\tau)\, d\tau \qquad (67)$$

with

$$R^\varepsilon(\sigma,\tau)\psi \;=\; A\; U^\varepsilon_A(\tau)\, U^\varepsilon_B(\sigma)\psi \;-\; U^\varepsilon_B(\sigma-\tau)\; A\; U^\varepsilon_{A+B}(\tau)\psi$$

for $\psi\in\mathcal{H}^4_2$. Since $U^\varepsilon_B(\sigma):\mathcal{H}^4_2\to\mathcal{H}^4_2$, the first term of the difference defining $R^\varepsilon(\sigma,\tau)\psi$ is differentiable with respect to σ and τ. For differentiability of the second term, we show $A: D_2\to D(B)$. Let $\varphi\in D_2$. We have $(A+B)^2\,\varphi$, $A^2\,\varphi$, $B^2\,\varphi\in L^2(\mathbb{R}^2,\mathbb{C}^2)$, and therefore also $(AB+BA)\varphi\in L^2(\mathbb{R}^2,\mathbb{C}^2)$. Moreover, $AB+BA=[A,B]+2BA=-\frac{\varepsilon i}{2}V(-i\varepsilon\nabla)+2BA$ on D_2, and thus $BA\,\varphi\in L^2(\mathbb{R}^2,\mathbb{C}^2)$, which implies $A\,\varphi\in D(B)$. Altogether, the mapping $(\sigma,\tau)\mapsto R^\varepsilon(\sigma,\tau)\psi$ is continuously differentiable for $\psi\in\mathcal{H}^4_2$, and Taylor expansion around $(0,0)$ gives a point $(\sigma_*,\tau_*)\in[0,\Delta_t]^2$, such that

$$R^\varepsilon(\Delta_t,\tau)\psi \;=\; \Delta_t\,\partial_\sigma R^\varepsilon(\sigma_*,\tau_*)\psi + \tau\,\partial_\tau R^\varepsilon(\sigma_*,\tau_*)\psi\,.$$

Moreover, for $\psi\in\mathcal{H}^4_2$ there exists $C^\varepsilon_\psi>0$ such that $\|R^\varepsilon(\Delta_t,\tau)\psi\|_{L^2}\le C^\varepsilon_\psi\,\Delta_t$, which gives the claimed

$$\|U^\varepsilon_{A+B}(\Delta_t)\psi - T^\varepsilon_{\Delta_t}\psi\|_{L^2} \;\le\; C^\varepsilon_\psi\,\Delta_t^2\,.$$

Second Step. Analysing C^ε_ψ for $\psi\in\mathcal{H}^6_3$, we study the derivatives of $R^\varepsilon(\sigma,\tau)\psi$ in more detail. Starting with $\partial_\sigma R^\varepsilon(\sigma_*,\tau_*)\psi$, we have to look at $A\,U^\varepsilon_B(\sigma_*)\,B\,\psi$ and $B\,A\,U^\varepsilon_{A+B}(\tau_*)\,\psi$. We have

$$\|\, B[A,U^\varepsilon_B(\sigma_*)]\psi\,\|_{L^2} \;\le\; \tfrac12\,\sigma_*\sup_{\sigma\in[0,\sigma_*]}\|\,B\,V(-i\varepsilon\nabla)\,U^\varepsilon_B(\sigma)\psi\,\|_{L^2}\,,$$

since

$$\begin{aligned} B[A,U^\varepsilon_B(\sigma_*)]\psi &= B\,U^\varepsilon_B(\sigma_*)\int_0^{\sigma_*}\tfrac{d}{d\sigma}\left(U^\varepsilon_B(-\sigma)\,A\,U^\varepsilon_B(\sigma)\psi\right)\,d\sigma\\ &= \tfrac{i}{\varepsilon}\,B\,U^\varepsilon_B(\sigma_*)\int_0^{\sigma_*}U^\varepsilon_B(-\sigma)\,[B,A]\,U^\varepsilon_B(\sigma)\psi\,d\sigma\,. \end{aligned}$$

We have for $\psi \in \mathcal{H}_3^\epsilon$ that $\psi \in C^4(\mathbb{R}^2, \mathbb{C}^2)$ and $|\psi(q)| \le |q|^{-3}$ for large q. Hence, by partial integration

$$\begin{aligned}
&\int_{\mathbb{R}^2} |q|^2\, |V(-i\varepsilon\nabla)\psi(q)|^2\, dq \\
&\quad = \int_{\mathbb{R}^2} \big(-i\varepsilon\, V(q)\, V(-i\varepsilon\nabla)\psi(q) + |q|^2\,(-\varepsilon^2\Delta)\psi(q)\big)\cdot \overline{\psi}(q)\, dq \\
&\quad \le \|B\psi\|_{L^2}\,(\|A\psi\|_{L^2} + \|\psi\|_{L^2}) + \|\,|q|^2\,\psi\|_{L^2}\|A\psi\|_{L^2}\,,
\end{aligned}$$

which implies $V(-i\varepsilon\nabla) : \mathcal{H}_3^\epsilon \to D(B)$. Using $[B, V(-i\varepsilon\nabla)] = -2\,i\varepsilon$, we therefore obtain by the same argument as before

$$\|\, B^k\,[V(-i\varepsilon\nabla), U_B^\varepsilon(\sigma)]\psi\,\|_{L^2} \;\le\; 2\sigma\|B^k\psi\|_{L^2}\,, \quad k \in \{0,1\}\,, \quad \sigma \in [0, \sigma_*]$$

for $\psi \in \mathcal{H}_3^\epsilon$. All these commutator bounds together yield

$$\begin{aligned}
\|A\,B\,U_B^\varepsilon(\sigma_*)\psi\|_{L^2} &\le \tfrac{\varepsilon}{2}\,\|V(-i\varepsilon\nabla)\,U_B^\varepsilon(\sigma_*)\psi\|_{L^2} + \|BA\,U_B^\varepsilon(\sigma_*)\psi\|_{L^2} \\
&\le \varepsilon\,\sigma_*\,\|\psi\|_{L^2} + \tfrac{\varepsilon}{2}\,\|V(-i\varepsilon\nabla)\,\psi\|_{L^2} \\
&\quad + \tfrac{\sigma_*}{2} \sup_{\sigma\in[0,\sigma_*]} \|\,B\,V(-i\varepsilon\nabla)\,U_B^\varepsilon(\sigma)\psi\,\|_{L^2} + \|BA\psi\|_{L^2} \\
&\le_c (\,\|\psi\|_{L^2} + \|A\psi\|_{L^2} + \|B\psi\|_{L^2} + \|B\,V(-i\varepsilon\nabla)\psi\|_{L^2} + \|BA\psi\|_{L^2}) \\
&\le_c \sum_{k+l=0}^{2} \|A^k\,B^l\psi\|_{L^2}\,.
\end{aligned}$$

Now we turn to $B\,A\,U_{A+B}^\varepsilon(\tau_*)\,\psi$ for $\psi \in \mathcal{H}_3^\epsilon$. Writing

$$(A+B)^3 = A^3 + B^3 + (A+2B)[A,B] + 3(A+B)BA + [A,B]B + [B,A]A\,,$$

we see $(A+B)BA\psi \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ for $\psi \in \mathcal{H}_3^\epsilon$ and obtain

$$\big\|\,[BA, U_{A+B}^\varepsilon(\tau_*)]\psi\,\big\|_{L^2} \;\le\; \tfrac{1}{2}\,\tau_* \sup_{\tau\in[0,\tau_*]} \|\,(V(-i\varepsilon\nabla)A + B\,V(-i\varepsilon\nabla))\;U_{A+B}^\varepsilon(\tau)\psi\,\|_{L^2}\,.$$

Moreover,

$$\begin{aligned}
\big\|\,[V(-i\varepsilon\nabla)A, U_{A+B}^\varepsilon(\tau)]\psi\,\big\|_{L^2} &\le \tau \sup_{\sigma\in[0,\tau]} \|\,A\,U_{A+B}^\varepsilon(\sigma)\psi\,\|_{L^2}\,, \\
\big\|\,[A, U_{A+B}^\varepsilon(\sigma)]\psi\,\big\|_{L^2} &\le \tfrac{\tau}{2} \sup_{s\in[0,\sigma]} \|V(-i\varepsilon\nabla)U_{A+B}^\varepsilon(s)\psi\,\|_{L^2}\,, \\
\big\|\,[V(-i\varepsilon\nabla), U_{A+B}^\varepsilon(\sigma)]\psi\,\big\|_{L^2} &\le 2\,\|\psi\|_{L^2}\,,
\end{aligned}$$

and

$$\big\|\,[B\,V(-i\varepsilon\nabla), U_{A+B}^\varepsilon(\tau)]\psi\,\big\|_{L^2} \;\le_c\; \|(A+B)\psi\,\|_{L^2}\,.$$

Putting all these pieces together, we obtain

$$\begin{aligned}
&\|B\,A\,U_{A+B}^\varepsilon(\tau_*)\,\psi\|_{L^2} \;\le_c \\
&\quad \big(\,\|A^2\psi\|_{L^2} + \|AB\psi\|_{L^2} + \|BA\psi\|_{L^2} + \|A\psi\|_{L^2} + \|B\psi\|_{L^2} + \|\psi\|_{L^2}\,\big)\,.
\end{aligned}$$

Having dealt with the σ-derivative, we now turn to $\partial_\tau R^\varepsilon(\sigma_*,\tau_*)$. Bounding this term requires additional bounds for $A^2\, U^\varepsilon_B(\sigma_*)\psi$ and $A\, U^\varepsilon_{A+B}(\tau_*)(A+B)\psi$ for $\psi \in \mathcal{H}^6_3$. We have

$$\big\|\, [A^2, U^\varepsilon_{A+B}(\sigma_*)]\psi \,\big\|_{L^2} \;\le\; \sigma_* \sup_{\sigma\in[0,\sigma_*]} \|V(-i\varepsilon\nabla)\, A\, U^\varepsilon_{A+B}(\sigma)\psi\|_{L^2}\,,$$

and therefore

$$\|A^2\, U^\varepsilon_{A+B}(\sigma_*)\,\psi\|_{L^2} \;\le_c\; \big(\|A^2\psi\|_{L^2} + \|A\psi\|_{L^2} + \|\psi\|_{L^2}\big)\,.$$

Moreover,

$$\|A\, U^\varepsilon_{A+B}(\tau_*)(A+B)\psi\|_{L^2} \;\le_c\; \sum_{k+l=0}^{2} \|A^k\, B^l\, \psi\|_{L^2}\,,$$

and therefore, $\|\partial_\sigma R^\varepsilon(\sigma_*,\tau_*)\psi\|_{L^2},\ \|\partial_\tau R^\varepsilon(\sigma_*,\tau_*)\psi\|_{L^2} \;\le_c\; \varepsilon^{-1}\sum_{k+l=0}^{2}\|A^k\, B^l\,\psi\|_{L^2}$. We finally obtain

$$C^\varepsilon_\psi \;=\; \text{const.}\ \varepsilon^{-2} \sum_{k+l=0}^{2} \|A^k\, B^l\, \psi\|_{L^2}\,.$$

□

18.2 Strang Splitting

Improving the convergence order of the Trotter splitting, a Strang splitting scheme is based upon the symmetrized operator

$$S^\varepsilon_{\Delta_t} \;:=\; \exp(-\tfrac{i}{\varepsilon}\tfrac{\Delta_t}{2}B)\,\exp(-\tfrac{i}{\varepsilon}\Delta_t\, A)\,\exp(-\tfrac{i}{\varepsilon}\tfrac{\Delta_t}{2}B)\,.$$

This scheme, introduced by G. Strang [St] in 1968, does not alter the computational effort, since it is realized by first applying $\exp(-\frac{i}{\varepsilon}\frac{\Delta_t}{2}B)$ to the initial data, followed by $M-1$ times $\exp(-\frac{i}{\varepsilon}\Delta_t\, B)\exp(-\frac{i}{\varepsilon}\Delta_t\, A)$, and then finally $\exp(-\frac{i}{\varepsilon}\frac{\Delta_t}{2}B)\exp(-\frac{i}{\varepsilon}\Delta_t\, A)$. Due to the symmetrization, there is an cancelation of the quadratic terms in Δ_t, and one obtains a convergence rate, which is cubic in the ratio Δ_t/ε. However, the improved convergence rate has to be paid by more regularity and decay of the data.

Proposition 11 (Strang Splitting) *For all parameters $\varepsilon > 0$ and all wave functions $\psi \in \mathcal{H}^8_4 := \{\psi \in H^8(\mathbb{R}^2,\mathbb{C}^2) \mid |q|^4\,\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)\}$ there exists a positive constant $C^\varepsilon_\psi > 0$ such that for all time steps $\Delta_t \in \mathbb{R}$*

$$\Big\|\exp(-\tfrac{i}{\varepsilon}\,\Delta_t\,(-\tfrac{\varepsilon^2}{2}\Delta + V))\psi - S^\varepsilon_{\Delta_t}\psi\,\Big\|_{L^2(\mathbb{R}^2)} \;\le\; C^\varepsilon_\psi\,|\Delta_t|^3\,.$$

For $\psi \in \mathcal{H}^{10}_5 := \{\psi \in H^{10}(\mathbb{R}^2,\mathbb{C}^2) \mid |q|^5\,\psi \in L^2(\mathbb{R}^2,\mathbb{C}^2)\}$ and $|\Delta_t| \le \text{const.}\,\varepsilon$ we have

$$C^\varepsilon_\psi \;=\; \text{const.}\ \varepsilon^{-3} \sum_{k+l+m=0}^{4} \big(\|A^k\, B^l\, A^m\,\psi\|_{L^2(\mathbb{R}^2)} + \|B^k\, A^l\, B^m\,\psi\|_{L^2(\mathbb{R}^2)}\big)\,.$$

PROOF. We use the notation introduced in the proof of Proposition 10. Let $\psi \in \mathcal{H}_4^8$. Studying the norm of the difference $U_{A+B}(\Delta_t)\psi - S^\varepsilon_{\Delta_t}\psi$, one inserts $U^\varepsilon_{A+B}(\frac{\Delta_t}{2})\psi$, denotes

$$\phi := U^\varepsilon_{A+B}(\Delta_t)\,\psi\,,$$

and uses the unitarity of the groups, to obtain

$$\begin{aligned}&\big\|U^\varepsilon_{A+B}(\Delta_t)\psi - S^\varepsilon_{\Delta_t}\psi\big\|_{L^2} = \\ &\quad \big\|\big(U^\varepsilon_A(-\tfrac{\Delta_t}{2})U^\varepsilon_B(-\tfrac{\Delta_t}{2})\phi - U^\varepsilon_{A+B}(-\tfrac{\Delta_t}{2})\phi\big) - \big(U^\varepsilon_A(\tfrac{\Delta_t}{2})U^\varepsilon_B(\tfrac{\Delta_t}{2})\psi - U^\varepsilon_{A+B}(\tfrac{\Delta_t}{2})\psi\big)\big\|_{L^2}\,.\end{aligned}$$

Repeating the first arguments of Proposition's 10 proof yields

$$\big\|U^\varepsilon_{A+B}(\Delta_t)\psi - S^\varepsilon_{\Delta_t}\psi\big\|_{L^2} \;=\; \varepsilon^{-1}\,\Big\|\int_0^{-\frac{\Delta_t}{2}} R^\varepsilon(-\tfrac{\Delta_t}{2},\tau)\phi\,d\tau - \int_0^{\frac{\Delta_t}{2}} R^\varepsilon(\tfrac{\Delta_t}{2},\tau)\psi\,d\tau\Big\|_{L^2} \tag{68}$$

with

$$R^\varepsilon(\sigma,\tau)f \;=\; A\,U^\varepsilon_A(\tau)\,U^\varepsilon_B(\sigma)f \;-\; U^\varepsilon_B(\sigma-\tau)\,A\,U^\varepsilon_{A+B}(\tau)f\,,\quad f\in\{\phi,\psi\}\,.$$

The function $\tau \mapsto R^\varepsilon(\mp\frac{\Delta_t}{2},\tau)f$ is twice continuously differentiable, since $\phi,\psi \in D_4 := D((A+B)^4) \supset D_3$. Second order Taylor expansion around $\tau = \mp\frac{\Delta_t}{2}$ in both integrals leaves us in the zeroth order term with

$$\begin{aligned}&\tfrac{\Delta_t}{2\varepsilon}\,\|R^\varepsilon(-\tfrac{\Delta_t}{2},-\tfrac{\Delta_t}{2})\phi + R^\varepsilon(\tfrac{\Delta_t}{2},\tfrac{\Delta_t}{2})\psi\|_{L^2} \;\le \\ &\quad \tfrac{\Delta_t}{2\varepsilon}\,\|\,A\,U^\varepsilon_{A+B}(-\tfrac{\Delta_t}{2})\phi - A\,U^\varepsilon_A(-\tfrac{\Delta_t}{2})U^\varepsilon_B(-\tfrac{\Delta_t}{2})\phi\|_{L^2} + \\ &\qquad\qquad \tfrac{\Delta_t}{2\varepsilon}\,\|\,A\,U^\varepsilon_{A+B}(\tfrac{\Delta_t}{2})\psi - A\,U^\varepsilon_A(\tfrac{\Delta_t}{2})U^\varepsilon_B(\tfrac{\Delta_t}{2})\psi\|_{L^2}\,.\end{aligned}$$

The two summands are operator A times differences of the form, which we have already encountered in equation (67). Expressing these differences in integral form, we obtain as integrands continously differentiable functions

$$(\sigma,\tau) \mapsto A^2\,U^\varepsilon_A(\tau)\,U^\varepsilon_B(\sigma)f - A\,U^\varepsilon_B(\sigma-\tau)\,A\,U^\varepsilon_{A+B}(\tau)f\,. \tag{69}$$

evaluated at $\sigma = \mp\frac{\Delta_t}{2}$ with $f \in \{\phi,\psi\}$. Therefore, first order Taylor expansion of these functions around $(0,0)$ gives a constant $C^\varepsilon_\psi > 0$ such that

$$\tfrac{\Delta_t}{2\varepsilon}\,\|R^\varepsilon(-\tfrac{\Delta_t}{2},-\tfrac{\Delta_t}{2})\phi + R^\varepsilon(\tfrac{\Delta_t}{2},\tfrac{\Delta_t}{2})\psi\|_{L^2} \;\le\; C^\varepsilon_\psi\,|\Delta_t|^3\,.$$

Since

$$\begin{aligned}\partial_\tau R^\varepsilon(\mp\tfrac{\Delta_t}{2},\mp\tfrac{\Delta_t}{2})f \;&=\; -\tfrac{i}{\varepsilon}\,A^2\,U^\varepsilon_A(\mp\tfrac{\Delta_t}{2})\,U^\varepsilon_B(\mp\tfrac{\Delta_t}{2})f \\ &\quad -\tfrac{i}{\varepsilon}\,B\,A\,U^\varepsilon_{A+B}(\mp\tfrac{\Delta_t}{2})f + \tfrac{i}{\varepsilon}\,A\,(A+B)\,U^\varepsilon_{A+B}(\mp\tfrac{\Delta_t}{2})f\,,\end{aligned}$$

the first order term in the second order Taylor expansions inside the integrals of equation (68) contributes

$$\begin{aligned}&\big(\tfrac{\Delta_t}{2\varepsilon}\big)^2\,\big\|A^2\,U^\varepsilon_B(-\tfrac{\Delta_t}{2})U^\varepsilon_A(-\tfrac{\Delta_t}{2})\phi - A^2\,U^\varepsilon_B(\tfrac{\Delta_t}{2})U^\varepsilon_A(\tfrac{\Delta_t}{2})\psi\,\big\|_{L^2} \le \\ &\quad \big(\tfrac{\Delta_t}{2\varepsilon}\big)^2\,\big\|A^2\,U^\varepsilon_B(-\tfrac{\Delta_t}{2})U^\varepsilon_A(-\tfrac{\Delta_t}{2})\phi - A^2\,U^\varepsilon_{A+B}(-\tfrac{\Delta_t}{2})\phi\,\big\|_{L^2} \\ &\qquad + \big(\tfrac{\Delta_t}{2\varepsilon}\big)^2\,\big\|A^2\,U^\varepsilon_{A+B}(\tfrac{\Delta_t}{2})\psi - A^2\,U^\varepsilon_B(\tfrac{\Delta_t}{2})U^\varepsilon_A(\tfrac{\Delta_t}{2})\psi\,\big\|_{L^2}\,.\end{aligned}$$

Recycling the preceding arguments once more, first order Taylor expansion around $(0,0)$ now for the function

$$(\sigma,\tau) \mapsto A^3\, U^\varepsilon_A(\tau)\, U^\varepsilon_B(\sigma) f - A^2\, U^\varepsilon_B(\sigma-\tau)\, A\, U^\varepsilon_{A+B}(\tau) f\,, \quad f \in \{\phi,\psi\} \tag{70}$$

yields

$$\left(\tfrac{\Delta_t}{2\varepsilon}\right)^2 \left\| A^2\, U^\varepsilon_B(-\tfrac{\Delta_t}{2}) U^\varepsilon_A(-\tfrac{\Delta_t}{2})\phi - A^2\, U^\varepsilon_B(\tfrac{\Delta_t}{2}) U^\varepsilon_A(\tfrac{\Delta_t}{2})\psi \right\|_{L^2} \;\le\; C^\varepsilon_\psi\, \Delta_t^4\,.$$

The second order term in the second order Taylor expansion contributes

$$\left(\tfrac{\Delta_t}{2\varepsilon}\right)^3 \left\| \partial^2_\tau R^\varepsilon(-\tfrac{\Delta_t}{2},\tau_-)\phi + \partial^2_\tau R^\varepsilon(\tfrac{\Delta_t}{2},\tau_+)\psi \right\|_{L^2} \;\le\; C^\varepsilon_\psi\, |\Delta_t|^3$$

with $\tau_\mp \in [-\frac{\Delta_t}{2}, \frac{\Delta_t}{2}]$, which yields the claimed

$$\| U^\varepsilon_{A+B}(\Delta_t)\psi - S^\varepsilon_{\Delta_t}\psi \|_{L^2(\mathbb{R}^2)} \;\le\; C^\varepsilon_\psi\, |\Delta_t|^3\,.$$

Before starting to analye the dependance of C^ε_ψ on $\varepsilon > 0$ and $\psi \in \mathcal{H}^{10}_5$, we give a look-up table of the commutators already derived in the proof of Proposition 10. We will use the shorthand $\nabla_\varepsilon := V(-i\varepsilon\nabla)$.

$[A,B]$	$[B,\nabla_\varepsilon]$	$[A,B\,A]$	$[B,B\,A]$	$[B,\nabla_\varepsilon\, A]$	$[A,B\,\nabla_\varepsilon]$	$[B,B\,\nabla_\varepsilon]$	$[A^2,B]$
$-i\frac{\varepsilon}{2}\,\nabla_\varepsilon$	$-2i\varepsilon$	$-i\varepsilon\nabla_\varepsilon A$	$-i\varepsilon B\,\nabla_\varepsilon$	$-i\varepsilon A$	$-i\varepsilon A$	$-i\varepsilon B$	$-i\varepsilon\nabla_\varepsilon A$

Firstly, we have to bound σ-derivatives of the functions in (69) and in (70), which means bounding

$$A^{2+k}\, B\, U^\varepsilon_B(\sigma)\psi\,, \quad A^{2+k}\, B\, U^\varepsilon_B(\sigma)\, U^\varepsilon_{A+B}(\Delta_t)\psi\,, \quad A^{1+k}\, B\, U^\varepsilon_B(\sigma-\tau)\, A\, U^\varepsilon_{A+B}(t)\psi$$

for $k \in \{0,1\}$, $\sigma,\tau \in [-\frac{\Delta_t}{2}, \frac{\Delta_t}{2}]$, $t \in \{\tau, \tau+\Delta_t\}$, and $\psi \in \mathcal{H}^{10}_5$. We have

$$\begin{aligned}&\|A^{2+k}\, B\, U^\varepsilon_B(\sigma)\psi\|_{L^2} \le_c \\ &\qquad \|B\psi\|_{L^2} + \|A\,B\psi\|_{L^2} + \|A^2\,B\psi\|_{L^2} + \|A^k\,B\psi\|_{L^2} + \|A^{1+k}\,B\psi\|_{L^2} + \|A^{2+k}\,B\psi\|_{L^2}\,,\end{aligned}$$

$$\begin{aligned}\|A^{2+k}\, B\, U^\varepsilon_B(\sigma)\, U^\varepsilon_{A+B}(\Delta_t)\psi\|_{L^2} \;&\le_c\; \|B\, U^\varepsilon_{A+B}(\Delta_t)\psi\|_{L^2} \\ &+ \|A\,B\,U^\varepsilon_{A+B}(\Delta_t)\psi\|_{L^2} + \|A^2\,B\,U^\varepsilon_{A+B}(\Delta_t)\psi\|_{L^2} + \|A^{2+k}\,B\,U^\varepsilon_{A+B}(\Delta_t)\psi\|_{L^2} \\ &\le_c \sum_{k+l=0}^{2} \|A^k\,B^l\,\psi\|_{L^2} + \|A^2\,B\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} + \|A^3\,B\psi\|_{L^2}\,,\end{aligned}$$

and

$$\begin{aligned}&\|A^{1+k}\,B\,U^\varepsilon_B(\sigma-\tau)\,A\,U^\varepsilon_{A+B}(t)\psi\| \le_c \\ &\qquad \|A^{1+k}\,U^\varepsilon_{A+B}(t)\psi\| + \|B\,A\,U^\varepsilon_{A+B}(t)\psi\| + \|A^{1+k}\,B\,A\,U^\varepsilon_{A+B}(t)\psi\| \le_c \\ &\qquad \sum_{k+l=0}^{2} \|A^k\,B^l\,\psi\| + \|A^2\,B\psi\| + \|A\,B\,A\,\psi\| + \|A^3\,\psi\| + \|A^2\,B\,A\psi\| + \|A^4\psi\|\,.\end{aligned}$$

Secondly, we have to bound the τ-derivatives of the functions in (69) and (70), which requires additional bounds on

$$A^{3+k}\, U_B^\varepsilon(\sigma)\psi\,, \quad A^{3+k}\, U_B^\varepsilon(\sigma)\, U_{A+B}^\varepsilon(\Delta_t)\psi\,, \quad A^{1+k}\, U_B^\varepsilon(\sigma-\tau)\, A\, U_{A+B}^\varepsilon(t)\,(A+B)\psi$$

for $k \in \{0,1\}$, $\sigma,\tau \in [-\frac{\Delta_t}{2}, \frac{\Delta_t}{2}]$, $t \in \{\tau, \tau+\Delta_t\}$, and $\psi \in \mathcal{H}_5^{10}$. We have

$$\|A^{3+k}\, U_B^\varepsilon(\sigma)\psi\|_{L^2} \;\leq_c\; \|\psi\|_{L^2} + \|A\,\psi\|_{L^2} + \|A^2\,\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} + \|A^{3+k}\,\psi\|_{L^2}\,,$$

and

$$\begin{aligned}
\|A^{3+k}\, U_B^\varepsilon(\sigma)\, U_{A+B}^\varepsilon(\Delta_t)\psi\|_{L^2} \;&\leq_c\; \|\psi\|_{L^2} + \|A\, U_{A+B}^\varepsilon(\Delta_t)\psi\|_{L^2} + \|A^2\, U_{A+B}^\varepsilon(\Delta_t)\psi\|_{L^2} \\
&\qquad + \|A^3\, U_{A+B}^\varepsilon(\Delta_t)\psi\|_{L^2} + \|A^{3+k}\, U_{A+B}^\varepsilon(\Delta_t)\psi\|_{L^2} \\
&\leq_c\; \sum_{k+l=0}^{2} \|A^k\, B^l\,\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} + \|A^{3+k}\,\psi\|_{L^2}\,.
\end{aligned}$$

Moreover,

$$\begin{aligned}
\|A^{1+k}\, U_B^\varepsilon(\sigma-\tau)\, A\, U_{A+B}^\varepsilon(t)\,(A+B)\psi\|_{L^2} \;&\leq_c\; \sum_{j=1}^{2+k} \|A^j\, U_{A+B}^\varepsilon(t)\,(A+B)\psi\|_{L^2} \\
&\leq_c\; \sum_{k+l=0}^{2} \|A^k\, B^l\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} + \|A^2\, B\psi\|_{L^2} + \|A^4\,\psi\|_{L^2} + \|A^3\, B\psi\|_{L^2}\,.
\end{aligned}$$

Finally, we need bounds for $\partial_\tau^2 R^\varepsilon$, which requires bounding

$$B^2\, A\, U_{A+B}^\varepsilon(t)\psi\,, \quad B\, A\, U_{A+B}^\varepsilon(t)(A+B)\psi\,, \quad A\, U_{A+B}^\varepsilon(t)(A+B)^2\psi$$

for $\sigma,\tau \in [-\frac{\Delta_t}{2}, \frac{\Delta_t}{2}]$, $t \in \{\tau, \tau+\Delta_t\}$, and $\psi \in \mathcal{H}_5^{10}$. We have

$$\|B^2\, A\, U_{A+B}^\varepsilon(t)\psi\|_{L^2} \;\leq_c\; \sum_{k+l=0}^{2} \|A^k\, B^l\,\psi\|_{L^2} + \|A\, B\, A\psi\|_{L^2} + \|B^2\, A\psi\|_{L^2}\,,$$

$$\begin{aligned}
\|B\, A\, U_{A+B}^\varepsilon(t)(A+B)\psi\|_{L^2} \;&\leq_c\; \sum_{k+l=0}^{2} \|A^k\, B^l\,\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} \\
&\quad + \|A\, B\, A\psi\|_{L^2} + \|B\, A\, B\psi\|_{L^2} + \|A^2\, B\psi\|_{L^2} + \|B\, A^2\psi\|_{L^2} + \|A\, B^2\psi\|_{L^2}\,,
\end{aligned}$$

and

$$\begin{aligned}
&\|A\, U_{A+B}^\varepsilon(t)(A+B)^2\psi\|_{L^2} \leq_c \\
&\qquad \sum_{k+l=0}^{2} \|A^k\, B^l\,\psi\|_{L^2} + \|A^3\,\psi\|_{L^2} + \|A\, B\, A\psi\|_{L^2} + \|B\, A^2\psi\|_{L^2} + \|B^2\, A\psi\|_{L^2}\,.
\end{aligned}$$

Thus, altogether we obtain

$$C_\psi^\varepsilon \;=\; \text{const.}\ \varepsilon^{-3} \sum_{k+l+m=0}^{4} \left(\|A^k\, B^l\, A^m\,\psi\|_{L^2} + \|B^k\, A^l\, B^m\,\psi\|_{L^2}\right)\,.$$

$\square$

19 Fourier Differencing

Since $V(q)$ is a trace-free symmetric matrix, its even powers are a multiple of the identity matrix. Hence, the application of $\exp(-\frac{i}{\varepsilon}\Delta_t B)$ is just multiplication with

$$\cos(\tfrac{1}{\varepsilon}\,\Delta_t|q|)\,\mathrm{Id} - \tfrac{i}{|q|}\sin(\tfrac{1}{\varepsilon}\,\Delta_t|q|)\,V(q)\,,$$

and it only remains to control the numerical error introduced by the realization of the semi-classical Laplacian. For this realization, we restrict ourselves to a compact computational domain $[-K,K]^2$ and regard the wave functions as $2K$-periodic in q_1- and q_2-direction. We denote

$$\mathcal{C}_{per}([-K,K]^2) := \left\{\psi \in C([-K,K]^2) \mid \psi(-K,\cdot) = \psi(K,\cdot)\,,\ \psi(\cdot,-K) = \psi(\cdot,K)\right\}$$

and define for $\psi \in \mathcal{C}_{per}([-K,K]^2)$ and $N \in \mathbb{N}$ the trigonometric interpolant

$$\psi_N(q) \;=\; \sum_{\|p\|_\infty \le N}{}'' \;\widehat{\psi}_p\,\exp(\,i\,\tfrac{\pi}{K}\,p\cdot q)\,, \qquad q \in [-K,K]^2\,.$$

The double-primed sum weighs summands having an index $p = (p_1,p_2) \in \mathbb{Z}^2$, such that exactly one component p_j statisfies $p_j \in \{\pm N\}$, with a factor $\frac{1}{2}$ and the summands having an index p with both $p_1,p_2 \in \{\pm N\}$ with a factor $\frac{1}{4}$. We require ψ_N to interpolate ψ for the $(2N+1)^2$ equally spaced points $q_n = \frac{K}{N}\,n$ with $n \in \mathbb{Z}^2$ and $\|n\|_\infty := \max_j |n_j| \le N$, which is satisfied by choosing the interpolation coefficients as

$$\widehat{\psi}_p \;=\; (2N)^{-2}\sum_{\|n\|_\infty \le N}{}''\;\psi(\tfrac{K}{N}\,n)\,\exp(-\,i\,\tfrac{\pi}{N}\,p\cdot n)\,, \qquad p \in \mathbb{Z}^2\,,\ \|p\|_\infty \le N\,.$$

In contrast to the interpolation coefficients $\widehat{\psi}_p$, we denote the Fourier coefficients of a function $\psi \in L^2([-K,K]^2)$ by $\widehat{\psi}(p)$ with

$$\widehat{\psi}(p) = (2K)^{-2}\int_{[-K,K]^2} \psi(q)\,e^{-\,i\,\frac{\pi}{K}\,p\cdot q}\,dq\,, \qquad p \in \mathbb{Z}^2\,.$$

Approximating the Laplacian $-\varepsilon^2\Delta\,\psi$ by

$$-\varepsilon^2\Delta\,\psi_N(q) \;=\; \varepsilon^2\,(\tfrac{\pi}{K})^2\sum_{\|p\|_\infty \le N}{}''\;|p|^2\,\widehat{\psi}_p\,\exp(\,i\,\tfrac{\pi}{K}\,p\cdot q)\,, \qquad q \in [-K,K]^2\,,$$

we obtain the following lemma.

Lemma 22 (Fourier Differencing) *Let $s \ge 2$. There exists a positive constant $C = C(s) > 0$ such that for all $\psi \in H^s(]-K,K[^2) \cap \mathcal{C}_{per}([-K,K]^2)$*

$$\|\,\varepsilon^2\Delta\,\psi - \varepsilon^2\Delta\,\psi_N\|_{L^2([-K,K]^2)} \;\le\; C\,(\varepsilon\,N)^{2-s}\,K^{s-1}\,\|\psi\|_{H^{\varepsilon,s}(]-K,K[^2)}$$

with $\|\psi\|^2_{H^{\varepsilon,s}(]-K,K[^2)} := \sum_{p\in\mathbb{Z}^2}(1+\varepsilon|p|)^{2s}\,|\widehat{\psi}(p)|^2$ the semi-classically scaled Sobolev norm.

The following proof is a semi-classical, two-dimensional version of Lemma 2.2 in [Ta], which can be regarded as a corollary of Bernstein's theorem. The imposed regularity of ψ guarantees, that the standard one-dimensional arguments apply with minor modifications.

PROOF. By the Sobolev imbedding theorem, the function ψ is Lipschitz continuous of any order $\lambda \in]0,1[$. Choosing $\lambda > \frac{1}{2}$, Bernstein's theorem, see for example Theorem 3.1 in Chapter VI of [Zy], provides absolute convergence of the one-dimensional Fourier series

$$\sum_{p_1=-\infty}^{\infty} \int_{-K}^{K} \psi(y_1, q_2)\, e^{-i\frac{\pi}{K} p_1 y_1}\, dy_1\, e^{i\frac{\pi}{K} p_1 q_1}, \quad \sum_{p_2=-\infty}^{\infty} \int_{-K}^{K} \psi(x_1, y_2)\, e^{-i\frac{\pi}{K} p_2 y_2}\, dy_2\, e^{i\frac{\pi}{K} p_2 q_2}$$

for every $q_1, q_2 \in [-K, K]$, and therefore by the dominated convergence theorem pointwise convergence of the two-dimensional Fourier series

$$\psi(q) \;=\; \sum_{p\in\mathbb{Z}^2} \widehat{\psi}(p)\, e^{i\frac{\pi}{K} p\cdot q}, \quad q \in [-K, K]^2 .$$

We get for $p \in \mathbb{Z}^2$ with $\|p\|_\infty \le N$ the so-called aliasing identity

$$\widehat{\psi}_p \;=\; (2N)^{-2} {\sum_{\|n\|_\infty \le N}}'' \sum_{l\in\mathbb{Z}^2} \widehat{\psi}(l)\, \exp(\, i\, n\cdot(l-p)\tfrac{\pi}{N}) \;=\; \sum_{l\in\mathbb{Z}^2} \widehat{\psi}(p + 2\,N\,l) \tag{71}$$

Therefore,

$$\begin{aligned} \psi(q) - \psi_N(q) \;&=\; {\sum_{\|p\|_\infty \le N}}'' \big(\widehat{\psi}(p) - \widehat{\psi}_p\big)\, e^{i\frac{\pi}{K}\, p\, q} + {\sum_{\|p\|_\infty \ge N}}'' \widehat{\psi}(p)\, e^{i\frac{\pi}{K}\, p\, q} \\ &=\; -{\sum_{\|p\|_\infty \le N}}'' \sum_{l\neq(0,0)} \widehat{\psi}(p + 2\,N\,l)\, e^{i\frac{\pi}{K}\, p\, q} + {\sum_{\|p\|_\infty \ge N}}'' \widehat{\psi}(p)\, e^{i\frac{\pi}{K}\, p\, q} \end{aligned}$$

and by Plancherel's formula

$$\|\,\varepsilon^2 \Delta\,\psi - \varepsilon^2 \Delta\,\psi_N\|^2_{L^2([-K,K]^2)} =$$

$$(2K)^2 {\sum_{\|p\|_\infty \le N}}'' \varepsilon^4\, (\tfrac{\pi}{K})^4\, |p|^4 \,\Big|\sum_{l\neq(0,0)} \widehat{\psi}(p + 2\,N\,l)\Big|^2 + (2K)^2 {\sum_{\|p\|_\infty \ge N}}'' \varepsilon^4\, (\tfrac{\pi}{K})^4\, |p|^4 \big|\widehat{\psi}(p)\big|^2 .$$

Clearly, we have for $\|p\|_\infty \le N$

$$\begin{aligned} \Big|\sum_{l\neq(0,0)} \widehat{\psi}(p + 2\,N\,l)\Big|^2 \;&\le\; \sum_{l\neq(0,0)} (1 + \varepsilon|p + 2\,N\,l|)^{2s}\, |\widehat{\psi}(p + 2\,N\,l)|^2 \\ &\qquad \cdot \sum_{l\neq(0,0)} (1 + \varepsilon|p + 2\,N\,l|)^{-2s} \\ &\le\; \text{const.} \sum_{l\neq(0,0)} (1 + \varepsilon|p + 2\,N\,l|)^{2s}\, |\widehat{\psi}(p + 2\,N\,l)|^2 \\ &\qquad \cdot (\varepsilon N)^{-2s} \sum_{l\in\mathbb{Z}^2} (2\,|l| - 1)^{-2s} \end{aligned}$$

and thus a positive constant $C = C(s) > 0$

$$(2K)^2 \sum_{\|p\|_\infty \le N}{}'' \varepsilon^4 \left(\tfrac{\pi}{K}\right)^4 |p|^4 \Big| \sum_{l \ne (0,0)} \widehat{\psi}(p + 2N\,l) \Big|^2 \le$$

$$C\,K^{-2}\,(\varepsilon N)^{4-2s} \sum_{\|p\|_\infty \le N}{}'' \sum_{l \ne (0,0)} (1 + \varepsilon|p + 2N\,l|)^{2s}\, |\widehat{\psi}(p + 2N\,l)|^2 \le$$

$$C\,K^{-2}\,(\varepsilon N)^{4-2s}\,\|\psi\|^2_{H^{\varepsilon,s}(]-K,K[^2)}\,.$$

Using

$$\sum_{\|p\|_\infty \ge N}{}'' \varepsilon^4 K^{-4} |p|^4 |\widehat{\psi}(p)|^2 \le (\varepsilon K^{-1} N)^{4-2s}\, \|\psi\|^2_{H^{\varepsilon,s}(]-K,K[^2)}\,,$$

we obtain the claimed

$$\|\,\varepsilon^2 \Delta\psi - \varepsilon^2 \Delta\psi_N\|_{L^2([-K,K]^2)} \le C\,(\varepsilon N)^{2-s}\,K^{s-1}\,\|\psi\|_{H^{\varepsilon,s}(]-K,K[^2)}\,.$$

□

20 The Reference Solver

Our reference solver for the preliminary validation of the surface hopping algorithm is a Strang splitting scheme with Fourier differencing Laplacian. The wave function is treated as periodic on the computational domain $[-K, K]^2$. From Proposition 11 we infer that the time step Δ_t should be significantly smaller than the semi-classical parameter ε, since the cube $(\Delta_t/\varepsilon)^3$ of their ratio dominates the convergence rate. For smooth functions, the discretization error for Fourier differencing obtained in Lemma 22 is superpolynomial in N/ε, where $(2N + 1)^2$ is the number of grid points employed. Hence, N should be considerably larger than $1/\varepsilon$. Drawing from the standard knowledge on the numerical discretization of partial differential equations we have also looked to satisfy the Courant-Friedrichs-Lewy condition $\Delta_t \ll 1/N$. Summarizing, we have carried out the numerical computations such that time step Δ_t and mesh size $1/N$ satisfy

$$\Delta_t \ll \tfrac{1}{N} \ll \varepsilon\,.$$

The by far more sophisticated approach of T. Jahnke and C. Lubich for the numerical discretization of the ordinary differential equation $i\varepsilon \frac{d}{dt}\psi(t) = H(t)\psi(t)$, $\psi(0) = \psi_0 \in \mathbb{C}^2$, comes with a step size restriction $\Delta_t < \sqrt{\varepsilon}$, see [JaLu03]. The algorithm realizing the Strang splitting scheme with Fourier differencing reads as follows.

Reference Solver

1. Evaluate the initial datum $\psi_0^\varepsilon \in L^2(\mathbb{R}^2, \mathbb{C}^2)$ on an equally spaced Cartesian grid of $(2N+1)^2$ points discretizing the computational domain $[-K, K]^2$.

2. Fix the time interval $[0, T]$ and set the timestep $\Delta_t = \frac{T}{M}$. Perform the first half splitting step by multiplying the initial wave function with

$$E(\tfrac{\Delta_t}{2}) \;:=\; \cos(\tfrac{1}{\varepsilon}\,\tfrac{\Delta_t}{2}\,|q|)\,\mathrm{Id} - \tfrac{i}{|q|}\,\sin(\tfrac{1}{\varepsilon}\,\tfrac{\Delta_t}{2}\,|q|)\,V(q)\,.$$

3. Apply a two-dimensional fast Fourier transform (FFT), multiply by the matrix

$$f_{k,l} \;=\; \exp(-i\varepsilon\,\Delta_t\,(f_k + f_l))\,, \qquad k, l = 1, \ldots, 2N+1$$

with

$$f_k \;=\; -(\tfrac{\pi}{K})^2\,(0, 1, 4, \ldots, (N-1)^2, N^2, N^2, (N-1)^2, \ldots, 4, 1)\,,$$

apply an inverse FFT, and multiply by $E(\Delta_t)$.

4. Repeat the previous step $M-1$ times, for the last step, however, replace $E(\Delta_t)$ by $E(\Delta_t/2)$ when applying the exponential of the potential.

Figure 10: Strang splitting scheme with Fourier differencing.

Part F

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